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ATMOSPHERIC CHEMISTRY OF POTENTIAL EMISSIONS FROM FUEL CONVERSION FACILITIES

A Smog Chamber Study

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The atmospheric chemistry of chemical species that may be emitted from fuel conversion facilities were studied in smog chambers. Of 17 compounds assessed for ozone-forming potential, 6 compounds were selected along with a control species, propylene, for testing in the presence of nitrogen oxides in four outdoor smog chambers. Selected compounds were furan, pyrole, thiophene, methanethiol, methyl sulfide, and methyl disulfide. Multiday exposures were performed, and both static and transport conditions were simulated. Ozone and sulfur dioxide formation was examined. The behavior of the test compounds was compared to that of a surrogate urban mix.

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ABSTRACT

The atmospheric chemistry of chemical species that may be emitted from fuel conversion facilities was studied in smog chambers. One hundred and six bag experiments and 20 smog chamber experiments were performed. A screening program was conducted using 125-liter Teflon bags as reactors to assess the ozone-forming potential of 17 compounds, which were candidates for smog chamber testing. From these 17 compounds, 6 compounds and a control species, propylene, were selected for testing in the presence of nitrogen oxides in four outdoor smog chambers. The test compounds were: furan, pyrrole, thiophene, methanethiol, methyl sulfide, and methyl disulfide. Multiple-day exposures were performed, and both static and transport conditions were simulated. In addition to ozone, sulfur dioxide was produced as a secondary pollutant by the photooxidation of the sulfur-containing species.

The effect of dilution on both ozone and sulfur dioxide production was examined. The behavior of the test compounds was compared to that of a surrogate urban mix. Under the proper conditions, the six test compounds were found to produce net ozone levels in excess of 0.08 ppm on the second and third days in both static and dilution experiments. The atmospheric behavior of these compounds should be considered in detail if substantial anthropogenic emissions, such as may occur at fuel conversion facilities, are anticipated.

This report was submitted in fulfillment of Task B of Contract No. 68-02-2258 by the Research Triangle Institute under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period June 30, 1975, to June 30, 1977, and work was completed as of May 6, 1977.

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We gratefully acknowledge these individuals for their efforts in bringing this project to a successful conclusion.

SECTION 1

INTRODUCTION

During the next several decades, the use of coal, shale oil, and other fossil fuels is expected to increase in the United States to satisfy growing domestic energy needs. Many fossil fuels are dirty, bulky, and difficult to transport, and have low heat content in their raw, natural states. To make these raw fuels more acceptable, fuel-conversion processes are being planned and will soon be producing clean, high-energy gas, solid, and liquid synthetic fuels. Operations such as coal gasification and liquefaction, shale oil production, and petroleum refining will assume an increased role in future energy production.

Fuel conversion facilities are potential sources of atmospheric emissions. Contaminants such as mineral matter and sulfur-, nitrogen-, and oxygen-containing compounds are removed and transformed during the processing of raw fuels. Emissions of compounds derived from fuel contaminants are anticipated. In addition, emissions of species from the processing operations themselves are expected to be produced. These atmospheric emissions may include not only the commonly considered pollutants such as SO_x, NO_x, CO, and hydrocarbons, but other compounds not previously considered from either the toxic or ozone-generative viewpoint. It is, therefore, necessary that the impact of synthetic-fuels processing on air quality be considered.

The literature survey, conducted as the first task of this contract and published as a companion document (ref. 1), addressed atmospheric emissions from coal gasification, coal liquefaction, shale oil production, and petroleum refining. The survey findings indicate that the same or similar chemical species are expected to be emitted from each of the four fuel-conversion operations. Compounds identified as potential emissions from fuel-conversion facilities are summarized as follows:

1. Sulfur-containing compounds will include SO_2, H_2S, thiols (mercaptans), sulfides, and thiophenes.

2. Nitrogen-containing compounds will include NO, NO_2, NH_3, HCN, and heteorocyclic species such as pyrroles and pyridines.
3. Organic compounds will include primarily volatile hydrocarbons up to C_{10}. Aromatic emissions such as benzene, toluene, and xylenes are anticipated. Other organics such as aldehydes, ketones, phenols, and polycyclic organic matter (POM) are expected.

For details concerning the fuel-conversion operations, chemical species, concentrations, and emission rates, the literature survey should be consulted (ref. 1).

The purpose of the task described in the present document was to study, by smog chamber simulation, the atmospheric chemistry associated with emissions from production and refining operations related to coal gasification, coal liquefaction, shale oil production, and petroleum refining. Since the impact on the air quality of both rural and urban areas of emissions from such operations may be very great, it is necessary to characterize their potential for air pollution and photochemical oxidant formation. A major objective was to examine the ozone-producing potential of selected chemical species and nitrogen oxides exposed to natural sunlight irradiation at ambient temperatures.

The approach devised consisted of the following four steps:

1. Identify and select several candidate compounds that are likely to be emitted from fuel conversion processes for experimental evaluation in smog chambers. Choose candidate compounds from the literature survey (ref. 1), focusing on those compounds or families of compounds whose ambient air chemistries have not been thoroughly investigated.
2. Devise and conduct a screening program using 125-l Teflon* bag reactors exposed to natural sunlight irradiation at ambient temperatures to assess relative reactivity based on ozone production of the selected candidate materials in the presence of nitrogen oxides.

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3. Based on the screening tests select compounds for investigation under static and simulated transport conditions in the four outdoor smog chambers comprising the RTI Smog Chamber Facility.
4. Conduct 3-day smog chamber tests on the selected compounds in the presence of NO_x. Choose test conditions which employ natural sunlight irradiation at ambient temperatures and which simulate both static (stagnant) and transport (dilution) atmospheric conditions.

SECTION 2

SUMMARY AND CONCLUSIONS

The atmospheric chemistry of 17 compounds was investigated in this study. One hundred and six bag experiments and 20 smog chamber experiments were performed. Many of the compounds were identified as potential air pollutants from production and refining operations related to coal gasification, coal liquefaction, shale oil production, and petroleum refining. The compounds selected for testing were: furan, pyrrole, thiophene, methanethiol, methyl sulfide, methyl disulfide, carbonyl sulfide, cyclopentadiene, 2-methyl furan, 2,5-dimethyl furan, 2-methyl thiophene, toluene, ethylbenzene, ortho-xylene, meta-xylene, para-xylene, and propylene. Propylene was included as a control.

Screening tests were performed to assess the ozone-forming potential of each of the above compounds. These experiments were conducted by irradiating air mixtures of the compound and nitrogen oxides in 125-l Teflon bag reactors under natural sunlight at ambient temperatures. Each compound was tested at two initial HC/NO_x ratios, 5 and 20. Target initial concentrations were 10 ppmC of the compound and 2.0 and 0.5 ppm of NO_x. The National Ambient Air Quality Standard (NAAQS) for photochemical oxidant, 0.08 ppm, was exceeded in at least one of the two test conditions for every compound tested except carbonyl sulfide and methanethiol. In addition, sulfur dioxide was observed as a product of photooxidation of each of the sulfur-containing compounds.

The following six compounds were chosen for additional bag studies and also for multiple-day smog chamber experiments: furan, pyrrole, thiophene, methanethiol, methyl sulfide, and methyl disulfide. As in the screening tests, propylene was chosen as a control compound for many of the bag and chamber experiments.

The stability of air mixtures of each of the six test compounds was evaluated in 125-l bag reactors both in the dark and under irradiation. All six test compounds were relatively stable in the dark, with half-lives of 3 days or longer. Exposure to sunlight enhanced the decay rates of each tested compound except methyl sulfide. Pyrrole and methyl disulfide exhibited half-lives of less than 1 day. Considerable quantities of SO_2 were observed as a product of irradiated air-methyl disulfide mixtures.

The dark phase reactivity of each of the six test compounds in the presence of O_3 was investigated in bags. Pyrrole and furan reacted rapidly with O_3. The rate constant determined for pyrrole was approximately the same as that determined for propylene. Among the sulfur-containing compounds, thiophene was the most reactive with O_3, and the alkyl sulfides were considerably less reactive.

Dark phase reactivity bag studies for each of the six test compounds were also conducted in the presence of NO_x. These experiments indicated that the test compounds were relatively unreactive with NO_x in the dark. Although the decay rate of pyrrole was enhanced somewhat by the presence of NO_2, half-lives for the test compounds were longer than 1 day. The NO_x decay rate was increased by a factor of three in the presence of furan. In general, however, nitrogen oxides behavior was not appreciably changed by the presence of the other five test compounds.

The behavior of the six test compounds in the ozone-potential screening tests indicated that each compound can participate in atmospheric photooxidation reactions. Many chemical reactions may contribute to the removal of the test compounds from the atmosphere, and the additional bag studies were conducted to determine the qualitative importance of four alternate pathways. Comparison of the findings indicated photooxidation to be a major pathway.

Multiple-day experiments in the four outdoor smog chambers comprising the RTI Smog Chamber Facility were conducted with furan, pyrrole, thiophene, methanethiol, methyl sulfide, methyl disulfide and the control hydrocarbon, propylene. Target initial conditions for these tests were 5.0 ppmC of the test compound and 1.0 ppm NO_x (20% NO_2). The design of the chamber facility provided for irradiation with natural sunlight at ambient temperature and also allowed the simulation of both static and transport (dilution) atmospheric conditions. Three test compounds were studied simultaneously, with one in each of the first three chambers; these results were compared with results of the control compound in the fourth chamber. Comparisons of these results were also made with results of runs conducted on other days with a simulated urban mix.

On the first day of a static run, thiophene was the slowest of the test compounds to reach NO-NO_2 crossover and required over 5 hours past dawn. The other test compounds required less than 3 hours. The ordering of the times to reach the maximum $[O_3]$ for the test compounds roughly duplicated that for the times to NO-NO_2 crossover. Thiophene, the slowest compound to crossover, achieved $[O_3]_{max}$ after 1500 EST, whereas the other five compounds reached $[O_3]_{max}$ by 1000.

With each of the test compounds, except the slow-reacting thiophene, NO_x was consumed more quickly than with propylene. Consumption of NO_x was very rapid in the alkyl sulfide runs; within an hour of the $[O_3]_{max}$, the NO_2 concentration had dropped to low levels, and approximately 90 percent of the initial NO_x had been consumed.

Each of the sulfur-containing species tested in the chambers produced SO_2 as a product of photooxidation on the first day of a static run. Substantial amounts of SO_2 were produced by the alkyl sulfides, whereas thiophene produced the smallest quantities of SO_2 of the sulfur-containing compounds tested in the chambers. Sulfur dioxide was detected as a reaction product simultaneously with the onset of NO oxidation. Concentration profiles indicate that the largest increase in $[SO_2]$ occurred between the time of NO-NO_2 crossover and the time of $[O_3]_{max}$, with the $[SO_2]_{max}$ occurring at approximately the same time as the $[O_3]_{max}$.

First, second, and third day behavior were compared using net ozone values ($\Delta O_3 = [O_3]_{max} - [O_3]_{min}$). The open-chain sulfur species produced not only ΔO_3 values of 0.4 to 0.7 ppm on the first day of static runs, but also considerable amounts of ozone on the second and third days. Thiophene, in contrast to the other test compounds, produced more ozone in static runs on both the second and third days than on the first day. In two static experiments with thiophene, a fivefold increase in ΔO_3 was observed from the first to the second day.

Each of the sulfur-containing compounds produced considerable quantities of SO_2 on the first day of a static run, whereas only thiophene produced significant levels on the second and third days. Of the compounds tested in the chambers, only the slow-reacting sulfur compound thiophene produced significant quantities of both O_3 and SO_2 in multiple-day irradiations. These findings suggest that, under stagnant conditions, large anthropogenic emissions of thiophene may reduce local air quality by increasing ambient levels of both O_3 and SO_2.

In dilution runs the chamber contents were diluted with purified air at a fixed rate starting at 0800 EST on the first day. The dilution rate was chosen so that after 24 hours of operation, 95 percent of the original chamber contents would be replaced by purified air. Dilution was terminated 24 hours after initiation, and the remaining 2 days of the run were conducted in the static mode. Under dilution conditions thiophene produced a first-day $[O_3]_{max}$ level over five times greater than the value achieved in the corresponding static run. Among the test compounds, however, this was the exception, and in general, dilution resulted in a slight reduction of the first day $[O_3]_{max}$.

Under dilution conditions, first day ΔO_3 levels were larger than the levels produced on the second and third days. This may suggest a decrease in ozone production on subsequent days downwind from sources of the tested compounds.

Second and third day ΔO_3 levels in dilution experiments were generally less than those in static runs. They were never reduced in proportion to the extent of dilution: ΔO_3 levels were generally reduced by less than 40 percent after 95 percent dilution. This finding demonstrates the nonlinear behavior of ozone formation in air parcels which experience dilution.

Dilution reduced $[SO_2]_{max}$ values achieved on the first day by the sulfur-containing species in comparison with static runs. Net SO_2 levels on the second and third days were reduced essentially to zero by dilution. The pronounced reductions of SO_2 levels achieved on each day of the multiple-day dilution runs reflects reactant-limited behavior on the resulting SO_2 formation. This may be contrasted with the nonlinear precursor-product relationship for ozone formation.

The test compounds with the exception of the control, propylene, produced ΔO_3 levels in excess of the NAAQS of 0.08 ppm on the second and third days in both static and dilution experiments. The atmospheric behavior of these compounds should, therefore, be considered in detail if significant anthropogenic sources, such as fuel conversion facilities, are to be constructed.

The results of this study suggest that, on a carbon basis, organosulfur compounds have similar ozone-generative potential as hydrocarbons normally recognized as ozone precursors. The experimental concentrations employed in this study were significantly higher than those anticipated in the atmosphere. If the demonstrated analogy between the ozone-generative potential of organosulfur compounds and hydrocarbons at high concentrations can be extrapolated to lower concentration levels, then these compounds should be considered as members of the nonmethane hydrocarbon class of oxidant precursors. On this basis it seems reasonable to assume that nonmethane hydrocarbon standards and control strategies aimed at oxidant control would maintain their current degree of effectiveness if the organosulfur species are included in the category of nonmethane hydrocarbons.

This research has also shown that organosulfur compounds in the presence of NO_x and sunlight are precursors of SO_2. Organosulfur compounds, therefore, should be considered in the development of future standards and control strategies for SO_2 and sulfates.

SECTION 3

RECOMMENDATIONS

Fuel conversion technology is in the early stages of its development. The identity and emission rates of organics emitted by fuel conversion processes are, therefore, poorly defined. Current estimates are based on engineering process flow diagrams, design material balances, and pilot plant results. Empirical emissions data are needed to supplement and verify current estimates. Large field programs encompassing both source sampling and ambient air monitoring should be mounted to identify and quantify emissions from pilot-, demonstration-, and commercial-size fuel conversion facilities. Research projects are currently underway to identify various emissions from laboratory-scale units. The Research Triangle Institute through EPA Grant No. 1394 (Pollutants from Synthetic Fuels Production) is conducting such a project with a small coal gasifier. Future atmospheric chemistry studies of emissions from such facilities should be coordinated closely with the above investigations.

This investigation has identified research areas which can be explored by smog chambers and by more fundamental chemical studies. The photochemistry of many of the test compounds is poorly defined over the range of wavelengths incident on the earth's surface: fundamental work is needed in this area. The hydroxyl radical is believed to be the dominant reactive species in photochemical smog reactions; other reactive species include ozone and atomic oxygen. Rate and mechanistic studies of the interactions of these reactive species with the test compounds are needed to provide a better understanding of the occurring chemistry and to allow computer simulation for predictive modeling.

This research has demonstrated the feasibility of using outdoor smog chambers to explore the atmospheric chemistry of selected chemical species. The feasibility of using small bag reactors for screening or special studies has also been demonstrated. The approach for future smog chamber investigations of potential emissions from fuel conversion facilities should be similar to that employed in the current study.

1. Use bag reactors to screen candidate compounds for subsequent smog chamber testing based on some criterion such as ozone-generative potential. Bag reactors can also be used for special stability or reactivity experiments.
2. Investigate the atmospheric chemistry of the selected compounds over multiple-day exposures in large outdoor smog chambers. Such experiments would be conducted with air-mixtures of the selected compound in the presence of nitrogen oxides. Results from these experiments could be used to define such first-day features as production surfaces for secondary pollutants such as ozone or in some cases SO_2. These experiments could be used to explore the effects of repeated diurnal cycles on ozone or SO_2 production.
3. Extend the experimental conditions employed in smog chambers to reflect more closely the chemical systems into which these compounds may be introduced. Experiments should be designed to explore the interaction of potentially emitted test species with other compounds. The following studies would be useful in this regard.
    (a) Explore the effects of adding the test compound to mixtures of a control hydrocarbon and NO_x. Two reference hydrocarbons could be used: a reactive hydrocarbon such as propylene or butene and a less reactive species such as propane or butane. Results of standard runs conducted simultaneously in both the presence and absence of the test compound could be compared to determine the presence or extent of synergistic behavior. This type of study should precede further studies described below.

    (b) Emissions from fuel conversion facilities will include species unique to the industry in addition to more commonly encountered compounds. One or more surrogate mixtures of fuel conversion emissions' compounds could be examined in smog chambers. Control strategies could be tested by varying the initial HC and NO_x concentrations, their ratio, or the relative amounts of the various species comprising the surrogate mixture.

(c) With the ever increasing demand for energy, it is unlikely that future fuel conversion facilities will be located in areas totally remote from urban centers. Emissions are, therefore, expected to become mixed with urban plumes after one or more days of transport. This scenario could be simulated by injecting a surrogate fuel conversion emissions mixture into smog chambers on the second day of experiments with a surrogate urban mix.

4. Investigate aerosol formation and behavior during the photooxidation of organic sulfur species. It is recognized that the introduction of SO_2 into a photochemically reactive HC-NO_x system will result in aerosol generation. Photochemically reactive systems of NO_x and sulfur-containing organic species were shown in the current study to generate SO_2. Simultaneous aerosol generation is also anticipated and should be examined.

The previous paragraphs have described in broad terms the types of studies that should be considered, based on the findings of this research. The specific recommendations which follow are suggested for consideration in the next phase of this research program.

1. Focus on one class of compounds such as sulfur-containing species.
2. Employ detection techniques specific for the class of compounds to be tested. Such a technique for sulfur species is gas chromatography with flame photometric detection.
3. Conduct smog chamber experiments with compounds selected from the following list of candidates. Although starred species were smog chamber test compounds in the present study, they may warrant additional investigation.

H_2S
COS
CS_2
*CH_3SH
C_2H_5SH
*CH_3SCH_3
$C_2H_5SCH_3$
$C_2H_5SC_2H_5$
*$(CH_3S)_2$
$(C_2H_5S)_2$
*Thiophene
2-Methylthiophene
3-Methylthiophene
2,5-Dimethylthiophene
Benzothiophenes

4. Conduct screening and special studies with selected compounds in bag reactors using the procedures developed in the current study.
5. Conduct smog chamber studies designed to address the key issues of ozone formation and SO_2 formation over multiple-day exposures. In addition, several of the candidate compounds may contribute to natural sulfur emissions, and these smog chamber studies may provide incidental data which can be used to elucidate the role of chemical or photochemical processes in the natural sulfur cycle.
6. Injection, sampling, or analytical difficulties prevented verification of initial injected concentrations of methanethiol; this should be resolved.
7. PAN determinations should be conducted to elucidate the NO_x consumptive mechanism which occurs during the photooxidation of the open chain sulfur species.
8. It is anticipated that the ultimate fate of sulfur-containing species in the atmosphere will be sulfate formation. Filter samples for subsequent X-ray fluorescent (XRF) analyses should be taken periodically during smog chamber runs. These data will allow the estimation of a sulfur balance and the fraction of sulfur in the particulate (and gas) phase.

SECTION 4

EXPERIMENTAL

OVERVIEW

This subsection describes the experimental design and also provides a general overview of the experiments conducted in this study. Table 1 identifies the compounds examined and provides a brief summary of the experimental program. Details concerning the apparatus, reagents, measurements, and procedures are provided in subsequent subsections.

The selection of compounds for experimental evaluation was based on the literature survey (ref. 1). The compounds listed in the first column of Table 1 were selected as candidates for smog chamber evaluation. The experimental program consisted of two phases: (1) screening studies aimed at selecting compounds for smog chamber evaluation and (2) the smog chamber studies.

The screening program was designed to assess the relative reactivity based on ozone production of the candidate compounds. Ozone-forming potential was evaluated in 125-l Teflon bag reactors for mixtures of each compound and NO_x (20% NO_2) at nominal initial HC/NO_x ratios of 5 and 20. Target initial concentrations of 10 ppmC of the candidate compound and either 2.0 or 0.5 ppm of NO_x were employed. Up to 10 bags could be tested simultaneously under identical environmental conditions for any 1-day exposure. This allowed fast and efficient screening of compounds for subsequent study in smog chambers. This program was also employed to identify incompatibilities between the subject compound and Teflon film, which should be considered prior to examination of the compound in the smog chamber facility.

Based on the results of the bag experiments, six compounds were selected for further examination in smog chambers (see Table 1). These compounds, however, were first subjected to additional experiments conducted in bag reactors. These experiments addressed the following points:

Table 1. EXPERIMENTAL PROGRAM

Compound Name	Compound Formula	Type of Experiment Conducted								
		Ozone-Forming Potential (Initial HC/NO$_x$∿5)	Ozone-Forming Potential (Initial HC/NO$_x$∿20)	Dark Stability	Light Stability	Dark Phase Reactivity with Ozone	Dark Phase Reactivity with NO$_x$	Smog Chamber Runs, Static	Smog Chamber Runs, Simulated Transport	
Furan	C_4H_4O	✓	✓	✓	✓	✓	✓	✓	✓	
Pyrrole	C_4H_5N	✓	✓	✓	✓	✓	✓	✓	✓	
Thiophene	C_4H_4S	✓	✓	✓	✓	✓	✓	✓	✓	
Methanethiol	CH_3-SH	✓	✓	✓		✓	✓	✓	✓	
Methyl sulfide	CH_3-S-CH_3	✓	✓	✓	✓	✓	✓	✓	✓	
Methyl disulfide	CH_3-S-S-CH_3	✓	✓	✓	✓	✓	✓	✓	✓	
Carbonyl sulfide	COS	✓	✓				✓			
Cyclopentadiene	C_5H_6	✓	✓							
2-Methylfuran	C_5H_6O	✓	✓							
2,5-Dimethylfuran	C_6H_8O	✓	✓							
2-Methylthiophene	C_5H_6S	✓	✓							
Toluene	C_7H_8	✓	✓							
Ethylbenzene	C_8H_{10}	✓	✓							
ortho-Xylene	C_8H_{10}	✓	✓							
meta-Xylene	C_8H_{10}	✓	✓							
para-Xylene	C_8H_{10}	✓	✓							
Propylene[1/]	CH_3-CH=CH_2	✓	✓			✓		✓	✓	

[1/] Propylene was employed as a control hydrocarbon in the smog chamber tests.

1. Dark phase stability of the selected compound in clean air,
2. Stability of the selected compound in clean air during and after 1 day of exposure to natural irradiation,
3. Dark phase reactivity of the selected compound and ozone in clean air,
4. Dark phase reactivity of the selected compound and NO_x in clean air.

Three-day smog chamber tests were conducted using the six compounds indicated in Table 1. These tests were conducted in the four outdoor smog chambers comprising the RTI Smog Chamber Facility. Target initial concentrations of 5 ppmC of the subject compound and 1 ppm of NO_x (20 percent NO_2) were employed. Three test compounds were studied simultaneously with one in each of the first three chambers. Propylene was employed in the fourth chamber as a control. Test conditions were used, which simulated static and transport atmospheric conditions.

APPARATUS

Two types of reactors were employed in this investigation: Teflon bag reactors and large, outdoor smog chambers. This equipment is described in the following paragraphs.

Teflon Bag Reactors

Clear plastic bags have been employed as photochemical reactors for outdoor irradiation in several studies (refs. 2, 3, 4). Bag reactors are economical and simple to fabricate. Reactor contents experience no dilution by sampling; therefore, measured concentrations require no correction for dilution.

The role of surface-mediated reactions in smog chamber investigations is unclear (ref. 5). Bufalini (ref. 6) has observed "memory" or "dirty chamber" effects for NO_x in glass, aluminum, and Teflon chambers. The excellent gas-phase nitrogen balance observed by Gay and Bufalini (ref. 7) in a Teflon bag suggests a reduced heterogeneous component for the Teflon surface as compared to glass. Although the level of trace contaminants varies from batch to batch, Teflon film may exhibit among the lowest levels of trace contaminant off-gassing of the materials commonly employed in photochemical smog studies (ref. 8). Teflon film also exhibits a reduced heterogeneous ozone-destructive potential. These considerations lead to the choice of Teflon film as the wall material for the RTI outdoor smog chambers (ref. 9). In view of the above points, Teflon film was also selected as the material of construction for the bag reactors in this study.

Twenty 125-l bags were fabricated from 0.05-mm (2 mil) thick fluorinated ethylenepropylene (FEP), Type A Teflon film. This material exhibits excellent light transmission in both the ultraviolet and visible regions of the solar spectrum incident on the earth's surface (ref. 10). Bag dimensions were approximately 0.9 m by 1.1 m, and the surface-to-volume ratio for each inflated bag was approximately 16 m^{-1}. The configuration of an inflated bag resembled that of a plump pillow.

After fabrication, the bags were "conditioned" in an attempt to lower the bag reactivity and reduce possible contamination by wall off-gassing. This was conducted by filling each bag with ozonized air to a concentration greater than 5 ppm, storing in the dark for one day, and flushing with clean air from the air supply.

A metal framework with a horizontal flexible "clothesline" was constructed to support 10 to 12 bags for simultaneous outdoor irradiations. The bag support was located in a grassy area within 10 to 15 m of the laboratory which housed the instruments and air supply system. The supporting line was about 9 m in length, oriented east to west, and configured at approximately 2 m from the ground. Each bag was suspended by two of its corners from the line. The bags were carried from the outdoor bag support into the laboratory for chemical analyses and then returned to the line. The length of time required for each battery of measurements was typically 15 to 20 minutes.

Air Supply--

The air supply for this study is illustrated in Figure 1. Commercially supplied compressed breathing grade air was purified before use by catalytic oxidation, Purafil[*] scrubbing, and drying with Drierite.[†]

The desired volume of air, 125 l, was introduced into each bag through its gas connection by a timed fill at a known flow rate. Flow rate from

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[*] Registered trademark of H.E. Burroughs and Associates.

[†] Registered trademark of the W. A. Hammond Drierite Company.

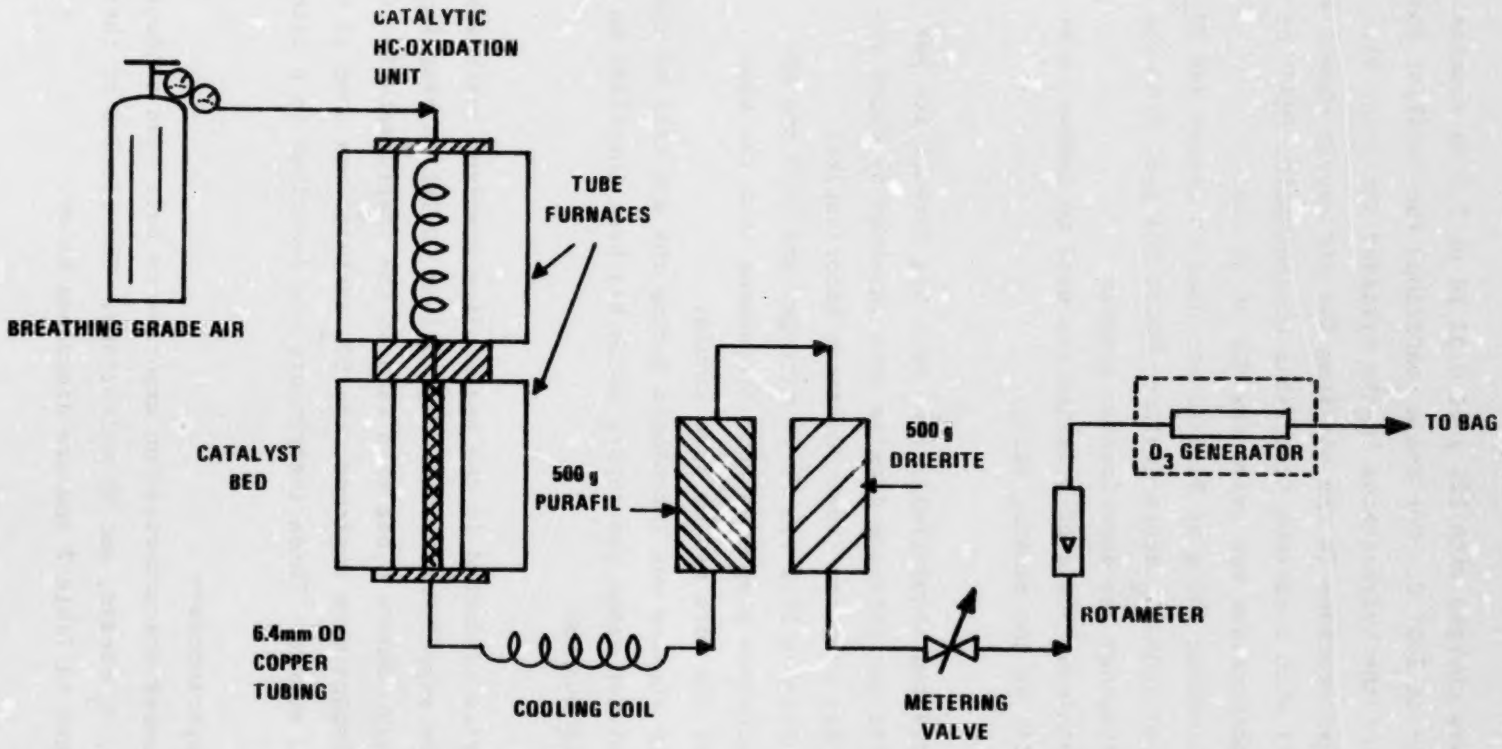
CATALYTIC
HC-OXIDATION
UNIT
TUBE
FURNACES
BREATHING GRADE AIR
CATALYST
BED
6.4mm OD
COPPER
TUBING
COOLING COIL
500 g
PURAFIL
500 g
DRIERITE
METERING
VALVE
ROTAMETER
O_3 GENERATOR
TO BAG

Figure 1. Air supply.

the air supply was monitored continually with a rotameter during each timed fill.

The catalyst bed was charged with 120 g of 0.5% Pd on 3.2 mm alumina spheres and was operated at 260° C. For these conditions the catalyst should oxidize 99.99+ percent of the hydrocarbons in the cylinder air (ref. 4). Analyses of C_2 to C_{10} hydrocarbons in the air from the air supply showed a maximum of 0.6 ppb (V/V) with a minimum detectable concentration (MDC) of 0.1 ppb (V/V). Methane concentration was below the MDC of 50 ppb.

A gas scrubber containing 500 g of Purafil was used to remove any NO_x contaminants. A measured zero NO_x concentration (MDC:0.001 ppm) from the air supply was observed throughout the experimental program.

A gas scrubber containing 500 g of Drierite was used to remove water desorbed from the Purafil by the passing air.

Injection System--

Pollutants were injected sequentially into each bag through its gas connection. Nitric oxide and nitrogen dioxide were injected by timed injections from commercially prepared (Scott Research Laboratories) certified cylinders containing 52.2 ppm NO in nitrogen and 52.3 ppm NO_2 in nitrogen. Test hydrocarbon compounds were introduced into the bags by syringe injections of the pure gas or pure liquid.

Ozone for the decay studies was introduced during the air fill by timed activation of an ultraviolet ozone generator, which had been installed in the air supply line for this purpose.

Sampling System--

The chemical analyses conducted in the bag studies involved instrumental methods. In most of the experiments a 1-m long, 3.2-mm OD Teflon sampling tube was used to manually connect a bag with each of the instruments in turn. Ozone, NO_x, and HC analyzers were employed. An SO_2 analyzer was used if the test compound contained sulfur. These instruments are described in a later section.

Bag Characterization Experiments--

Three types of chamber characterization experiments have been conducted: clean air irradiations, O_3 decays, and NO oxidations. The results of these experiments are presented in Table 2 and are discussed below.

The purpose of clean air irradiations is to determine the amount of ozone formed when purified air is irradiated in smog chambers. The ozone results from photochemical processes involving trace levels of nitrogen oxides and organics. These trace contaminants either remain in the air after purification or desorb from the walls of the reactor. Ozone levels of 0.013 and 0.034 ppm were formed during clean air irradiations conducted in bags (see Table 2). These results compare favorably with the values of 0.009, 0.033, and 0.034 ppm reported recently in a similar study (ref. 4), which also employed Teflon bag reactors.

Ozone can disappear inside a chamber by reacting heterogeneously with the walls or by reacting homogeneously with contaminants present inside the chamber. Ozone decay rates reported as half-lives under both dark conditions and irradiation have been used as measures of smog chamber reactivity. Based on this measure, Teflon bag reactors have been observed to be among the least reactive of current smog chambers with dark phase ozone half-lives of 45 to 150 hours and half-lives of 9 to 16 hours under exposure to natural irradiation (ref. 4). The reduced half-lives for irradiated conditions may be attributed mainly to secondary reactions following ozone photolysis. Dark phase half-life measurements were conducted for selected bags in the current study and yielded values of from 70 to 92 hours (see Table 2). These results are consistent with the previously referenced work and emphasize the reduced heterogeneous ozone-destructive potential of Teflon film.

The oxidation of NO should proceed in the dark by the third-order thermal reaction, $NO + NO + O_2 \rightarrow 2\ NO_2$. In the absence of reactive organic species, the above thermal reaction should be the major pathway for NO disappearance. Loss rates of NO under irradiation in excess of the thermal rate may be attributed to participation of organic contaminants in the normal photochemical NO-oxidation reactions. Dimitriades has suggested that the rate of NO loss under irradiated conditions provides a highly sensitive measure of chamber contamination levels (ref. 10). Nitric oxide oxidation experiments were conducted by injecting 80% NO and 20% NO_2 into bags containing 125 l of purified air. The bags were then either stored in the dark or exposed to sunlight. The apparent second order rate constants for NO disappearance were determined from the slope of $[NO]^{-1}$ vs. time plots. Ratios of experimentally determined rate constants to the established value (1.77×10^{-2} ppm^{-1} hr^{-1}

Table 2. BAG CHARACTERIZATION STUDIES

EXPERIMENT	RESULTS			
Clean Air Irradiation	Date	$[O_3]_{max}$1/		
	6-8-76	0.013		
	6-9-76	0.034		
Ozone Decay (Dark)	Date	$[O_3]_{initial}$1/	$t_{1/2}$2/	
	6-3 to 6-4-76	0.666	76	
	6-3 to 6-4-76	1.220	75	
	6-3 to 6-4-76	1.183	70	
	8-5-76	1.258	92	
NO Oxidations (Light and Dark)	Date	$[NO]_{initial}$1/	Exposure3/	k_{expt}/k_{therm}4/
	6-2-76	1.380	L	0.97
	6-8-76	1.626	L	0.83
	6-9-76	1.732	L	0.86
	6-17-76	1.062	D	1.56
	8-6-76	0.943	D	1.22

1/ Concentration units: ppm.

2/ Ozone half lives, $t_{1/2}$, are expressed in hours.

3/ "L" signifies that the bag was exposed to natural sunlight during the experiment; "D" signifies that the bag was stored in the dark during the experiment.

4/ k_{expt} is the rate constant calculated from the data assuming a second order reaction; k_{therm} is the established rate constant for the thermal oxidation of NO at 300° K (1.77×10^{-2} ppm^{-1} hr^{-1} [ref. 11]).

[ref. 11]) are presented in Table 2. These ratios range from 0.83 to 1.56 and suggest a low background reactivity for the bags in this study.

RTI Smog Chamber Facility

The Research Triangle Institute Smog Chamber Facility consists of four smog chambers (volume: 27 m^3; surface to volume ratio: 1.9 m^{-1}). Figure 2 illustrates the general design. The chambers are located outdoors, and irradiation is provided by natural sunlight. The walls are 0.13 mm thick (5 mil) FEP Teflon film supported by aluminum frames. The floors are 0.25 mm (10 mil) thick FEP Teflon film laid over a reflective layer of aluminum foil, which serves to raise the light intensity within the chambers and thus compensate for transmission losses through the walls. Mixing in each chamber is provided by a 0.45-m diameter aluminum fan blade on a shaft driven by a 185-W (1/4 hp) motor using a belt-pulley system.

Subsystems Comprising the Smog Chamber Facility--

In addition to the chambers proper, provisions were made for purification, reactant injection, and sample collection with subsequent instrumental and wet chemical analyses. The overall system is illustrated in Figure 3.

Air purification unit--Details of the air purification unit are shown in Figure 4. This unit has three modes of operation: purge, cleanup, and dilution.

During the purge mode, air is supplied by a blower from a 10-m meteorological tower. This air is then drawn through each chamber and exhausted at flow rates up to 0.34 $m^3\ min^{-1}$ by three two-stage diaphragm pumps. Purging may also be accomplished at higher flow rates, up to 2.3 $m^3\ min^{-1}$, by opening a manway in the floor and allowing the tower blower to force air through each chamber.

After purging with ambient air, the chambers are sealed, and air is recirculated through the purification unit in the cleanup mode. The purification unit contains the following equipment:

1. Desiccant column (6.5 kg of 4A molecular sieves),
2. Two HEPA particle filters,
3. Heated catalyst column (5 kg of 0.5 percent Pd on alumina catalyst; operating temperature: 200-475° C),
4. Air cooler,

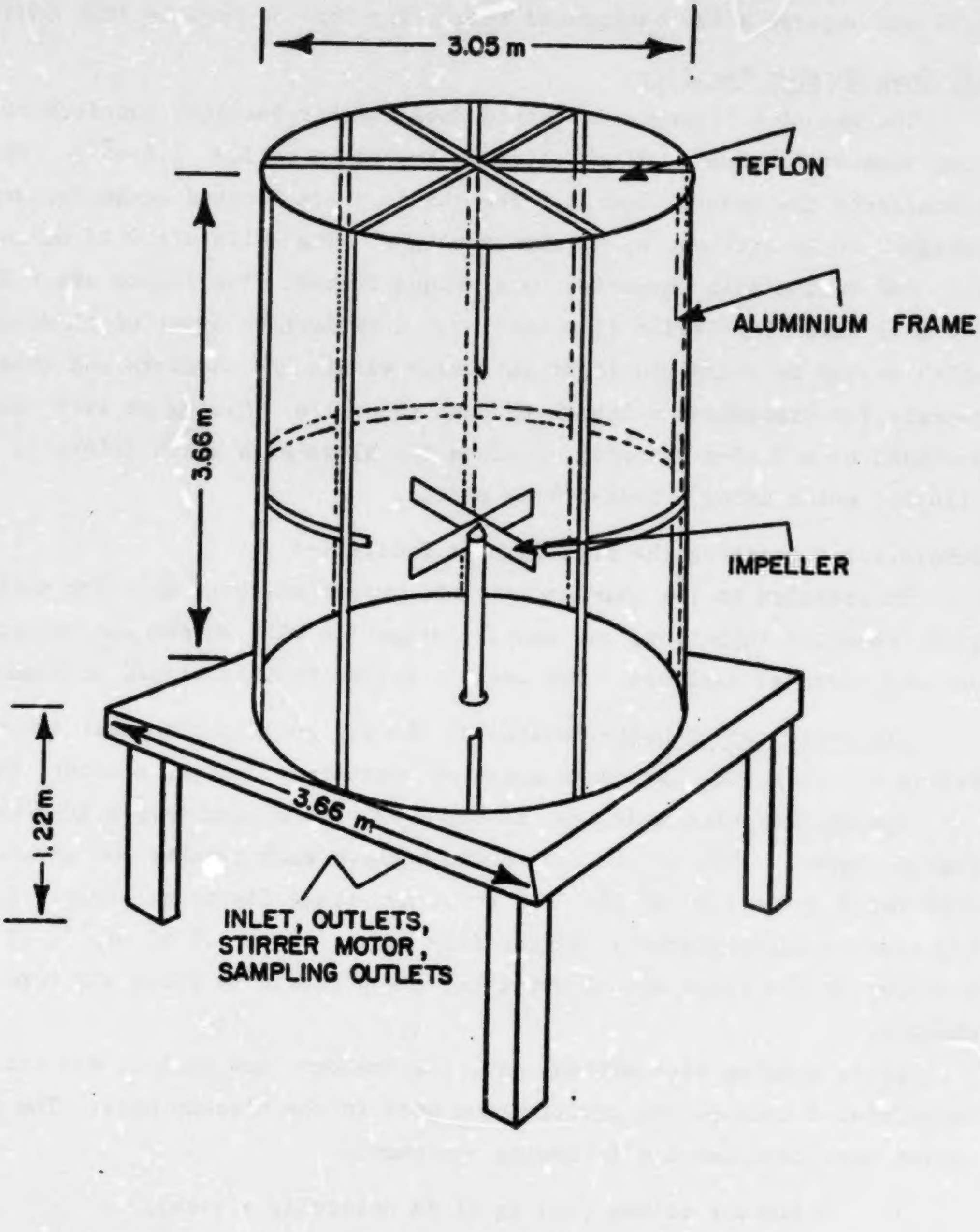
3.05 m
TEFLON
ALUMINIUM FRAME
3.66 m
IMPELLER
1.22 m
3.66 m
INLET, OUTLETS,
STIRRER MOTOR,
SAMPLING OUTLETS

Figure 2. A 27-cubic meter Teflon outdoor smog chamber.

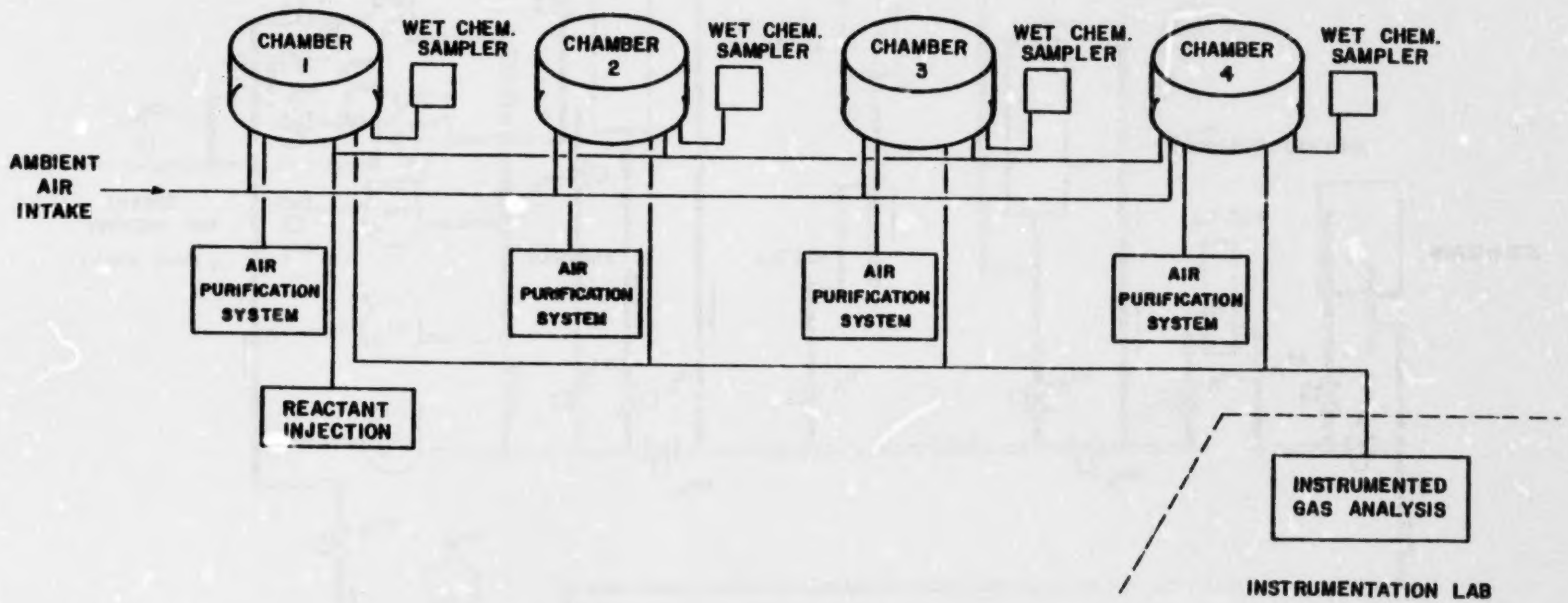
CHAMBER 1
WET CHEM. SAMPLER
CHAMBER 2
WET CHEM. SAMPLER
CHAMBER 3
WET CHEM. SAMPLER
CHAMBER 4
WET CHEM. SAMPLER
AMBIENT AIR INTAKE
AIR PURIFICATION SYSTEM
AIR PURIFICATION SYSTEM
AIR PURIFICATION SYSTEM
AIR PURIFICATION SYSTEM
REACTANT INJECTION
INSTRUMENTED GAS ANALYSIS
INSTRUMENTATION LAB

Figure 3. System diagram, RTI smog chambers.

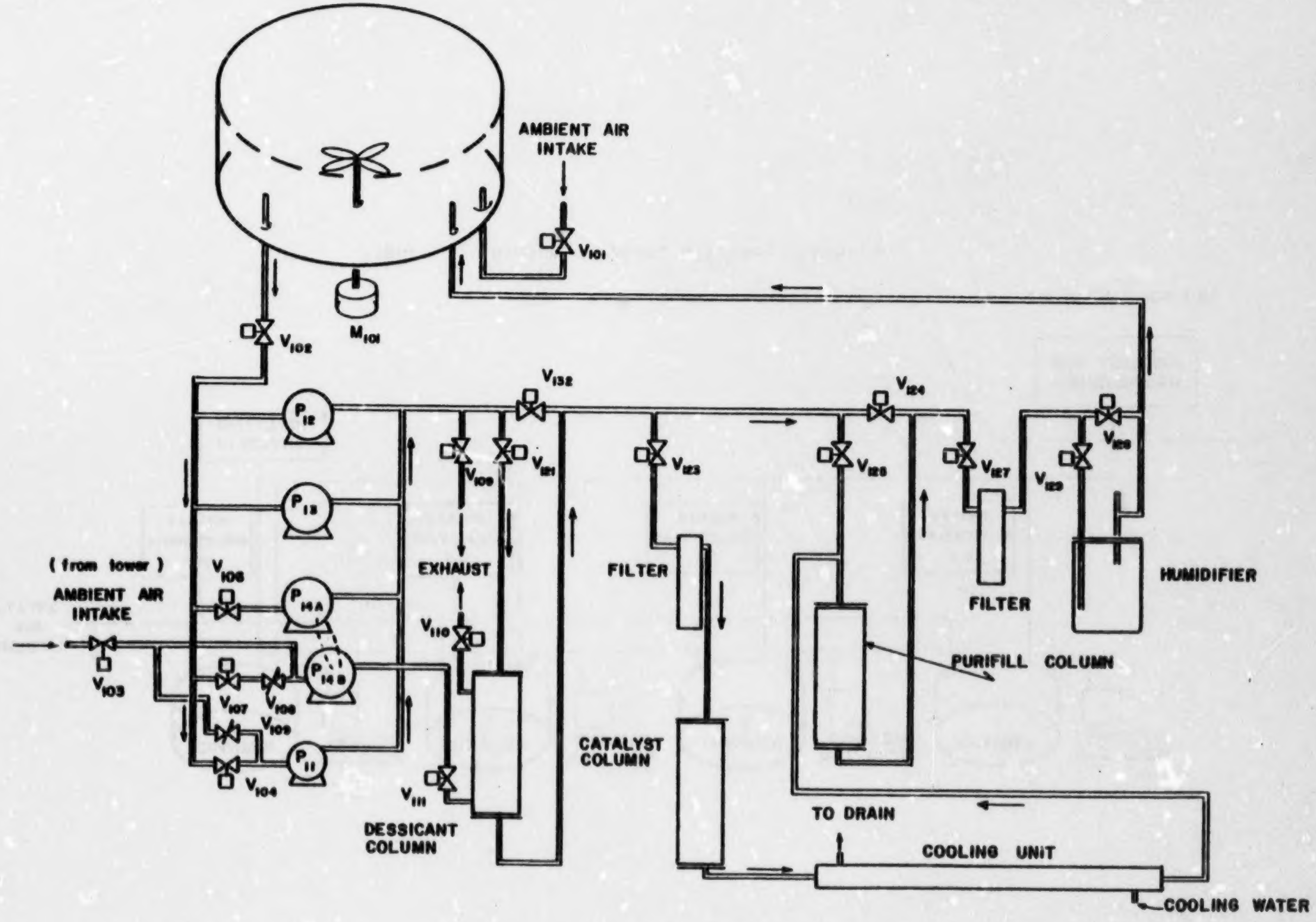
AMBIENT AIR
INTAKE
V_{101}
M_{101}
V_{102}
(from tower)
AMBIENT AIR
INTAKE
V_{103}
P_{12}
P_{13}
P_{14A}
P_{14B}
P_{11}
V_{106}
V_{107}
V_{108}
V_{109}
V_{104}
V_{109}
V_{121}
V_{132}
EXHAUST
V_{110}
V_{111}
DESSICANT
COLUMN
V_{123}
FILTER
CATALYST
COLUMN
V_{124}
V_{125}
V_{127}
V_{129}
V_{128}
FILTER
HUMIDIFIER
PURIFILL COLUMN
TO DRAIN
COOLING UNIT
COOLING WATER

Figure 4. ir purification unit, RTI smog chamber.

5. Purafil column (containing 6.5 kg of Purafil for NO_x and O_3 removal),
6. Humidifier.

Solenoid-driven valving allows the inclusion or exclusion of this equipment as may be appropriate in achieving desired experimental conditions. In this study, items 2, 3, 4, and 5 were included for cleanup and dilution operation. The purification or "cleanup" operation requires 8 to 12 hours at a flow rate of approximately 0.28 m^3 min^{-1}. Pollutant removal efficiency of the purification unit is discussed in a subsequent subsection.

To effect dilution, the chamber contents are recirculated through the purification unit at flow rates corresponding to the desired dilution rate. Flow rates for this operational mode are between 0.0085 and 0.058 m^3 min^{-1}. A flow rate recirculating through the purification unit of 0.058 m^3 min^{-1} was employed to simulate 95 percent dilution over 24 hours. Of course, the purification unit was not employed (zero flow rate) to simulate static conditions.

Injection system--A schematic of the reactant injection system is seen in Figure 5. There are three injection manifolds from cylinders of compressed gases. The flow rates are controlled by calibrated manual needle valves, and the quantity of each injection is controlled by timed, manual operation of the appropriate solenoid valves. Nitric oxide and NO_2 are injected sequentially from a single Teflon manifold. Hydrocarbons (propylene in this study) are injected from a copper manifold. Ozone may be added by injecting oxygen from a third manifold through an O_3 generator at each chamber; this feature is employed in O_3 decay experiments. After the reactants have been injected, each of the manifolds is flushed with nitrogen.

Pure gases such as methanethiol are introduced via syringe injection through a N_2-purged 1-m long, 4.8-mm ID TFE Teflon tube located under each chamber. This Teflon tube is also used for periodic grab sampling. Pure liquid compounds are injected as liquids from a precision gas-tight syringe with subsequent volatilization in a heated, stainless steel injection manifold. A schematic of the heated injection manifold is presented in Figure 6. Nitrogen is used as a purge gas to sweep the injected compound into the chamber.

Sampling System--The sampling system is illustrated in Figure 7. Automatic sampling from each chamber occurs at 10-minute intervals four times per hour.

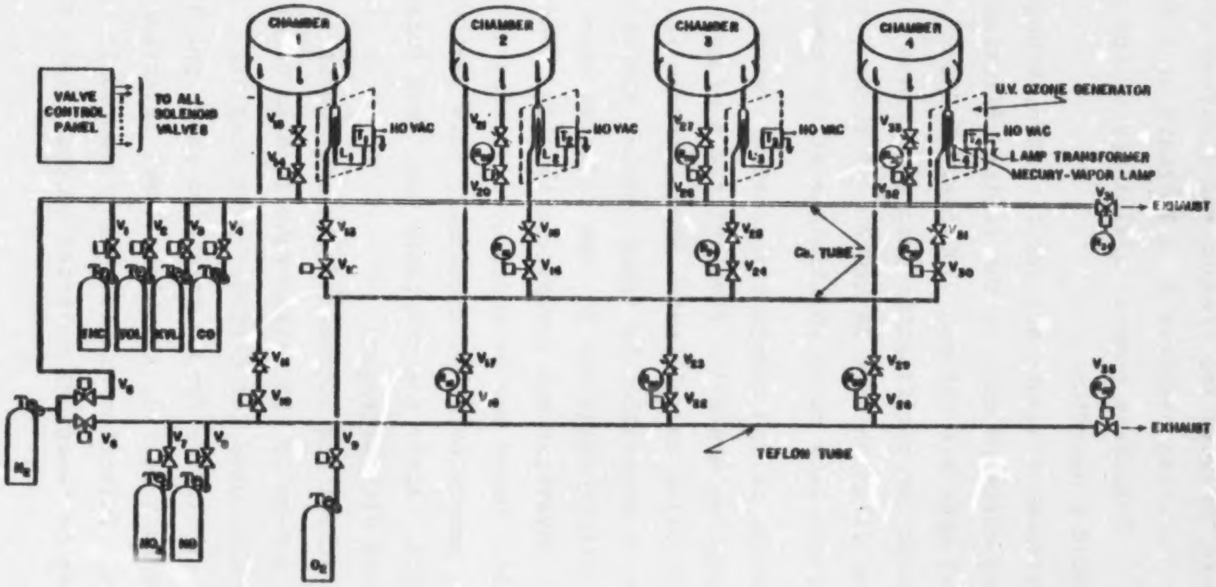
VALVE CONTROL PANEL
TO ALL SOLENOID VALVES
CHAMBER 1
CHAMBER 2
CHAMBER 3
CHAMBER 4
110 VAC
110 VAC
110 VAC
110 VAC
U.V. OZONE GENERATOR
LAMP TRANSFORMER
MECURY-VAPOR LAMP
EXHAUST
EXHAUST
Cu. TUBE
TEFLON TUBE
CO
N_2
NO_2
NO
O_2
V_1
V_2
V_3
V_4
V_5
V_6
V_7
V_8
V_9
V_{20}
V_{24}
V_{27}
V_{30}
V_{32}
V_{33}

Figure 5. Reactant injection system, RTI smog chambers.

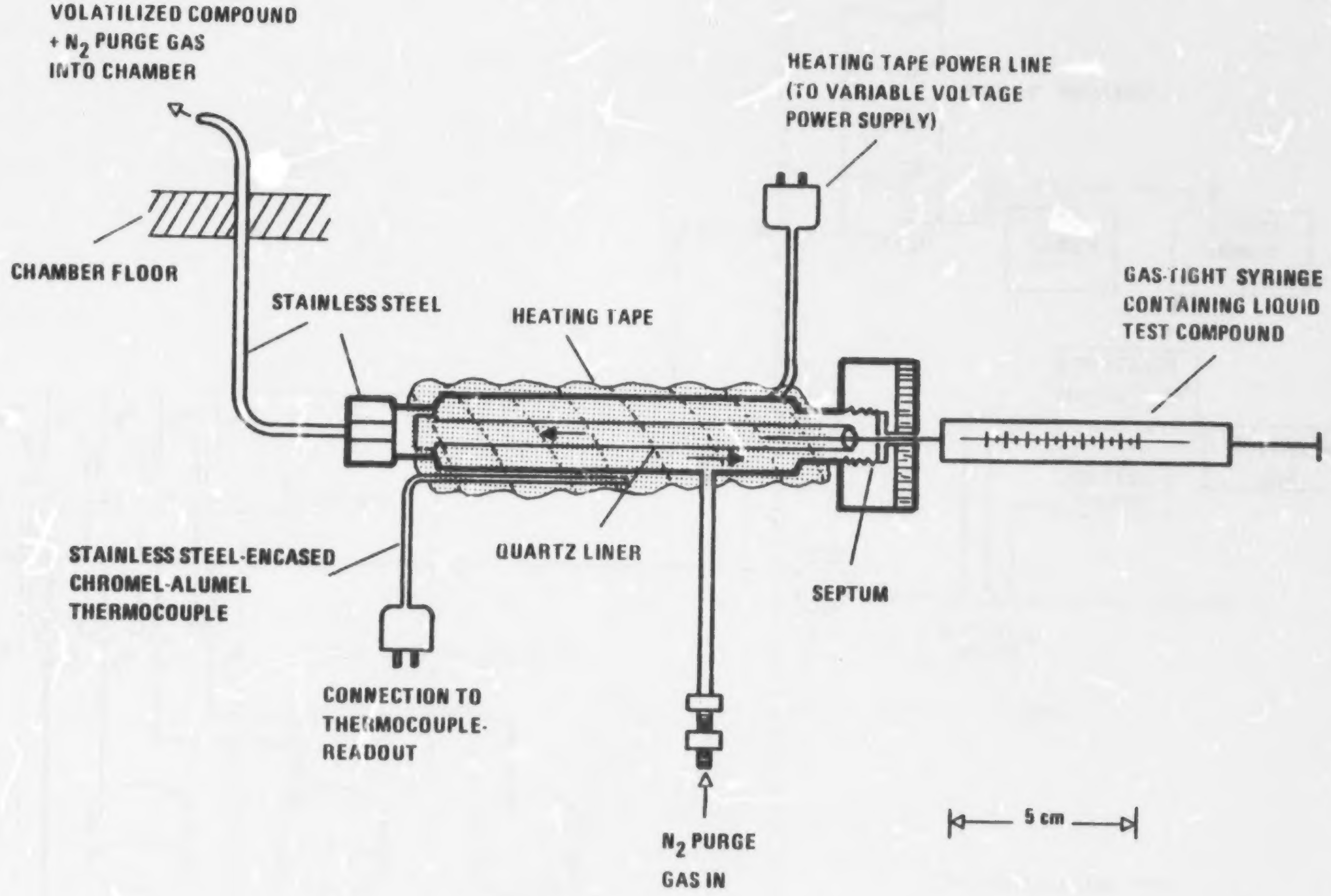
VOLATILIZED COMPOUND
+ N_2 PURGE GAS
INTO CHAMBER
HEATING TAPE POWER LINE
(TO VARIABLE VOLTAGE
POWER SUPPLY)
CHAMBER FLOOR
GAS-TIGHT SYRINGE
CONTAINING LIQUID
TEST COMPOUND
STAINLESS STEEL
HEATING TAPE
STAINLESS STEEL-ENCASED
CHROMEL-ALUMEL
THERMOCOUPLE
QUARTZ LINER
SEPTUM
CONNECTION TO
THERMOCOUPLE-
READOUT
5 cm
N_2 PURGE
GAS IN

Figure 6. Heated stainless steel manifold for volatilizing liquid test compounds prior to injection into a smog-chamber.

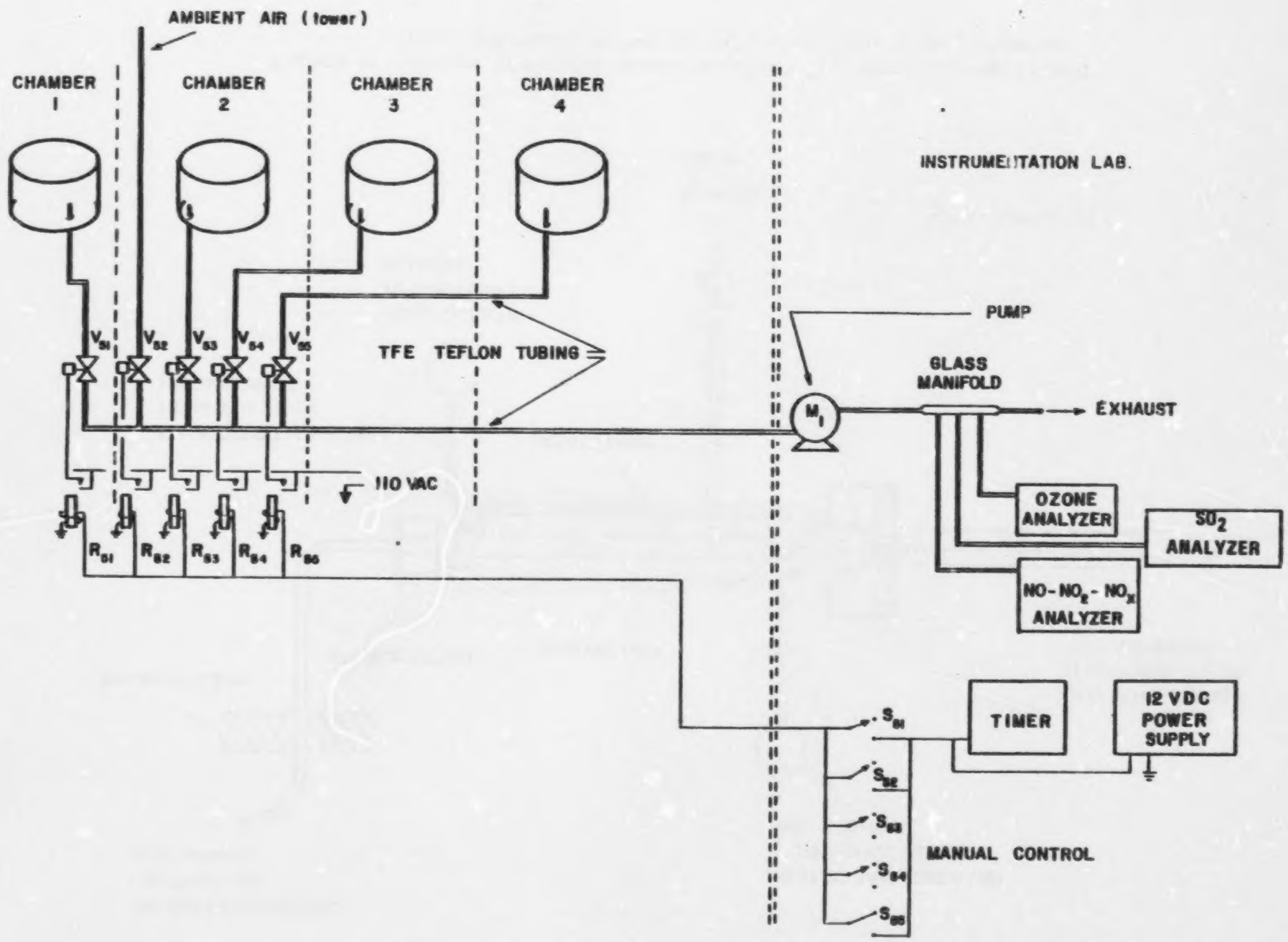
AMBIENT AIR (tower)
CHAMBER 1
CHAMBER 2
CHAMBER 3
CHAMBER 4
INSTRUMENTATION LAB.
V_{S1}
V_{S2}
V_{S3}
V_{S4}
V_{S5}
TFE TEFLON TUBING
PUMP
GLASS MANIFOLD
M_1
EXHAUST
110 VAC
R_{S1}
R_{S2}
R_{S3}
R_{S4}
R_{S5}
OZONE ANALYZER
SO_2 ANALYZER
$NO-NO_2-NO_X$ ANALYZER
TIMER
12 VDC POWER SUPPLY
S_{S1}
S_{S2}
S_{S3}
S_{S4}
S_{S5}
MANUAL CONTROL

Figure 7. Sampling system, RTI smog chambers.

An automatic timer activates the appropriate sampling solenoid valves and provides for a 10-minute sample from each chamber once per hour. During the remaining 20 minutes the operator is free to calibrate instruments, analyze bag samples, or allow the timer to automatically sample ambient air from the 10-m meteorological tower.

The sampled air must travel through 4.8-mm ID Teflon tubing for distances of 48 m from the most distant and 26 m from the nearest chamber to the laboratory. The sample is drawn at a flow rate of 0.005 m^3 min^{-1} (5 lpm) by a Metal-Bellows MB-41 pump and is delivered to a glass manifold in the laboratory from which the instruments draw their samples. These instruments include an O_3 analyzer, an $NO-NO_2-NO_x$ analyzer, and an SO_2 analyzer having a total volumetric flow requirement of 0.003 m^3 min^{-1} (3 lpm).

In addition to the automated sampling system described above, a 1-m long, 4.8-mm ID Teflon tube is located under each chamber for periodic manual grab sampling. Wet bubbler samples for oxidant, NO_2, and CH_2O determinations are collected at this location. Samples for subsequent hydrocarbon analyses are also collected at this point in 10-l Teflon bags. These samples are drawn through the 1-m long sampling tube with a Metal-Bellows MB-41 pump and exhausted into the Teflon bags. Typically, grab samples are collected manually twice a day from each chamber (at 0900 and 1600 EST).

Chamber Characterization--

Operating characteristics of the chambers comprising the RTI Smog Chamber Facility are documented in the following paragraphs. These points are reported to provide a basis for assessing the performance of the RTI chambers and to allow comparison with other chambers.

Mixing--As noted earlier, mixing in each chamber is provided by a fan designed for that purpose. Unless specified otherwise, the fan operates continually during each experiment.

Air velocity measurements have been conducted within each chamber. The minimum air velocity was measured to be greater than 0.05 m sec^{-1} within 0.02 m of the floor. Air velocities increased with distance from the walls to a maximum in excess of 4.0 m sec^{-1} near the moving fan blade.

If a smog chamber can be assumed to be an agitator-stirred tank, then a recently published relationship can be used to estimate the time required for complete mixing (ref. 12). This procedure indicates that mixing should be 90 percent complete within 24 seconds after injection of a pollutant.

Purification system--The air purification system routinely reduces the NO_x content of the purified air to a measured zero (MDC: 0.001 ppm). The catalytic hydrocarbon oxidation system typically reduces C_2 to C_{10} hydrocarbons measured by gas chromatography to less than 50 ppbC (MDC: 0.1 ppb [V/V]). Typical "postcleanup" hydrocarbon levels are shown in Table 3 for each chamber.

Dilution--The target recirculation flow rate through the purification unit employed in this study was 0.058 m^3 min^{-1}. This corresponds to 95 percent dilution in 24 hours and may be interpreted to mean that, after 24 hours of operation at this flow rate, 95 percent of an unreactive material initially present would be removed by the purification unit. A manual control valve (V108 in Figure 4) is used to set the recirculation flow rate through the purification unit. The valve setting is established manually prior to each run in which dilution is to be employed. Based on CO measurements, the target flow rate is expected to be achieved within ±20 percent.

Chamber tightness--Exchange of chamber contents with the ambient atmosphere is expected. Chamber leaks may be attributed to replacement of the volume required by sampling and to chamber "breathing" caused by diurnal temperature variations and buffeting by winds. The sampling flow rate of 0.005 m^3 min^{-1} for 10 minutes per hour corresponds to a dilution of 4.4 percent in 24 hours. Under static conditions, overall 24-hour exchange rates including the contribution due to sampling are expected to range from 15 to 35 percent based on the 24 percent maximum value recently reported (ref. 13) for chambers of similar construction. Leak tests using CO and Freon 12 as tracers have indicated that exchange rates generally fall within the expected range. The reported data have not been corrected for dilution.

Sample line losses--The most distant chamber is 48 m from the instruments in the laboratory. When NO, NO_2, and O_3 are present in the chamber, during periods of irradiation, a small reduction of NO and O_3 and a slight increase in NO_2 may occur due to reaction in the dark sample line (ref. 14). In view of the short residence time (10 seconds) this contribution should be small in most cases, and the data were not corrected for these effects.

Table 3. PREINJECTION HYDROCARBON ANALYSES (ppmC)

Chamber / Compound	No. 1			No. 2			No. 3			No. 4		
	4-23-76	8-3-76	8-24-76	4-23-76[2]	8-3-76	8-24-76	4-23-76	8-3-76	8-24-76	4-23-76	8-3-76	8-24-76
Ethane/Ethylene	0.034	0.004	0.008		0.010	0.012	0.050	0.005	0.016	0.005	0.011	0.007
Propane	0.001	—	—		0.002	0.002	0.002	—	0.002	—	—	0.002
Propylene	0.002	0.001	—		0.001	—	0.003	0.002	0.003	0.002	—	0.001
Acetylene	0.001	0.001	0.002		0.001	0.001	0.002	0.001	0.001	—	0.001	0.001
n-Butane	0.008	0.001	0.002		0.003	0.003	0.008	0.001	0.002	—	0.001	0.003
1-Butene	—[1]	—	—		—	—	—	—	—	—	—	—
2-Butene	—	0.004	—		0.011	—	—	0.003	—	—	0.002	—
i-Butane	0.010	—	—		0.001	—	—	0.001	—	—	—	—
i-Pentane	—	0.004	0.005		0.003	0.003	—	—	0.003	—	0.007	0.002
Cyclopentane	—	—	—		—	—	—	—	—	—	—	—
Toluene	—	—	—		—	—	—	—	—	—	—	—
SUM	0.056	0.016	0.017		0.032	0.021	0.065	0.013	0.027	0.007	0.023	0.016

[1] Entries denoted by blanks,"__", represent either nondetected concentrations or concentrations detected at less than 0.001 ppmC.

[2] Analysis not available.

The sampled air volume must pass through a considerable length of sampling line (26 to 48 m) and a pump before it is delivered to the instruments for analysis. Sample modification is therefore expected. Experiments were conducted to quantify these changes for O_3, NO, and NO_2. The losses were typically less than 5 percent; therefore no corrections were made to the data.

Grab samples for subsequent hydrocarbon analyses were collected at each chamber, were drawn through a 1-m long, 0.0048-m ID Teflon tube with a Metal-Bellows MB-41 pump, and were exhausted into 10-1 Teflon bags. An in-line MnO_2 scrubber, which was employed in a previous study (ref. 9) in an attempt to remove O_3 and stabilize hydrocarbon concentrations, was not used in this study. This measure was taken in view of a recent study (ref. 15), which indicated that MnO_2 is effective in oxidizing thiols to disulfides.

Characterization experiments--Three types of chamber characterization experiments have been conducted: clean air irradiations, O_3 decays, and NO oxidations. The results of these experiments are presented in Table 4. Similar characterization experiments were conducted for Teflon bag reactors; these results were discussed earlier.

The levels of background ozone formed in clean air irradiations conducted in the RTI smog chambers range from 0.04 to 0.14 ppm. The results of multiple-day experiments presented in Table 4 indicate that on the first day ozone levels near 0.08 ppm were achieved. The second- and third-day ozone concentrations slightly exceed the first-day levels. These background ozone levels compare favorably with the value of 0.14 ppm reported for the outdoor UNC facility (ref. 13) and the value of 0.10 ppm reported for the indoor Bureau of Mines chamber (ref. 10).

Examination of the ozone half-lives reported in Table 4 for the four RTI chambers indicates consistent behavior from chamber to chamber. Dark phase half-lives range from 18 to 37 hours, and light phase values range from 9 to 11 hours. These half-lives are greater than the values summarized recently for 10 indoor chambers (ref. 4). Although the ozone half-lives in the RTI facility are somewhat less than the values discussed earlier for Teflon bag reactors, the above comparisons indicate that the RTI chambers have a low reactivity with ozone.

Experimentally determined rate constants for NO oxidation have been divided by the established value for the second order thermal reaction

Table 4. CHAMBER CHARACTERIZATION EXPERIMENTS

EXPERIMENT	CHAMBER	RESULTS									
Clean Air Irradiations		4-6-76[1]		4-7-76		4-8-76		4-23-76[2]		4-24-76	
		$[O_3]_{max}$[3]	Time[4]	$[O_3]_{max}$	Time	$[O_3]_{max}$	Time	$[O_3]_{max}$	Time	$[O_3]_{max}$	Time
	1							0.101	1708	0.139	1508
	2	0.065	1538	0.094	1538	0.080	1538	0.040	1518	0.074	1518
	3	0.075	1558	0.115	1558	0.109	1558	0.073	1728	0.113	1528
	4							0.073	1838	0.116	1838

EXPERIMENT	CHAMBER	8-1-75		8-1-75		4-25 to 4-26-76	
Ozone Decays (Light and Dark)		$[O_3]_{initial}$[1]	$t_{1/2}$ (light)[5,6]	$[O_3]_{initial}$	$t_{1/2}$ (dark)[7]	$[O_3]_{initial}$	$t_{1/2}$ (dark)[8]
	1	0.600	9.8	0.829	21.8	0.735	25.4
	2	0.621	10.4	0.825	27.5	0.726	37.1
	3	0.609	10.8	0.823	23.1	0.563	18.4
	4	0.650	9.5	0.835	30.3	0.523	24.4

EXPERIMENT	CHAMBER	7-11-75		8-3 to 8-4-76	
NO Oxidations (Light and Dark)		$[NO]_{initial}$[1]	k_{expt}/k_{therm} (light)[9]	$[NO]_{initial}$	k_{expt}/k_{therm} (dark)[10]
	1	0.540	2.44	0.588	1.63
	2	0.569	0.94	0.675	1.37
	3	0.538	2.18	0.520	2.15
	4	0.575	2.01	0.622	1.61

[1] A three-day experiment.

[2] A two-day experiment.

[3] Concentration units: ppm.

[4] EST.

[5] Ozone half-lives, $t_{1/2}$, are expressed in hours.

[6] Experiment was conducted from 0900 until 1530 EST.

[7] Experiment was conducted from 0100 until 0530 EST.

[8] Experiment was conducted 2100 until 0330 EST.

[9] k_{expt} is the rate constant calculated from the data assuming a second order reaction; k_{therm} is the established rate constant for the thermal oxidation of NO at 300° K (1.77×10^{-2} ppm^{-1} hr^{-1} [ref. 11]); experiment was conducted from 0700 until 1330 EST.

[10] Experiment was conducted from 1900 until 0340 EST.

(1.77×10^{-2} ppm^{-1} hr^{-1} [ref. 11]). These ratios are presented in Table 4 and range from 0.9 to 2.5. They may be compared to the values of 4.0 for the Bureau of Mines chamber (ref. 10) and to values of 4.8 and 3.0 for the outdoor UNC facility (ref. 13). These comparisons emphasize the low background reactivity exhibited by the RTI Smog Chamber Facility.

REAGENTS

The reagents used in this study are listed in Table 5. Other information including boiling point, purity, injection mode, and supplier is also provided.

The single component gas and liquid reagents employed in this study were acquired from commercial suppliers with stated purities generally better than 95 percent. Dicyclopentadiene was "cracked" by distillation to cyclopentadiene (ref. 16) prior to injection. The other reagents were used without further purification.

Analyses of the gas mixtures reported by suppliers were confirmed in our laboratory. One of the propylene tanks, 294 ppm (V/V), was prepared at RTI by blending 99% propylene gas (Phillips Petroleum Company) with hydrocarbon-free air (Airco). The concentration was determined by gas chromatographic comparison with commercially supplied (Scott Research Laboratories) calibration mixtures of propylene and air.

Nitrogen used as a purge gas in bag and chamber studies was Matheson "Oxygen Free" grade. Air for the bag studies was delivered from the air supply. This catalytic air cleanup system was described in the "Apparatus" subsection. Air for the chamber studies was supplied from air purification systems, also described in the "Apparatus" subsection.

MEASUREMENT METHODS

The measurement methods employed in the bag and chamber studies are described below. A summary of these methods is presented in Table 6.

Bag Studies

Instrumental methods of chemical analysis were employed in the bag studies. Ozone, NO, NO_2, and the reactant hydrocarbon analyses were conducted routinely; sulfur dioxide was also measured if the reactant compound contained sulfur. These data are reported in Appendix B. A description of each analytical method is provided in the next subsection.

Table 5. REAGENTS

Reagent	b.p.[1] °C	Purity[2] %	Injection Mode[3]	Supplier
Furan	(32)	99^+	VL,L	Aldrich Chemical Company
Pyrrole	131	98	VL,L	Aldrich Chemical Company
Thiophene	83-85	NS[4]	VL,L	J. T. Baker Chemical Co.
Methanethiol	(7.6)	99.5	G	Matheson Gas Products
Methyl sulfide	38	98	VL,L	Aldrich Chemical Company
Methyl disulfide	109	NS	VL,L	Aldrich Chemical Company
Dicyclopentadiene[5]	170	95	L	Aldrich Chemical Company
2-Methylfuran	63-66	90	L	Aldrich Chemical Company
2,5-Dimethylfuran	92-94	99	L	Aldrich Chemical Company
2-Methylthiophene	113	95	L	Aldrich Chemical Company
Toluene	(110.6)	99	L	Fisher Scientific
ortho-Xylene	(144.4)	NS	L	Eastman Organic Chemicals
meta-Xylene	138-139	NS	L	Eastman Organic Chemicals
para-Xylene	(138)	NS	L	Eastman Organic Chemicals
Ethylbenzene	136	99	L	Aldrich Chemical Company
Carbonyl sulfide	(-48)	97.5	G	Matheson Gas Products
Propylene	(-47)	205±4 ppm (V/V) in air	GM	Scott Research Laboratories
Propylene	(-47)	294 ppm (V/V) in air	GM	RTI Blend
Nitric oxide (bag study)	(-152)	52.2±1 ppm in N_2	GM	Scott Research Laboratories
Nitric oxide (chamber)	(-152)	220 ppm in N_2	GM	Matheson Gas Products
Nitrogen dioxide (bag study)	(21.1)	52.3±1 ppm in N_2	GM	Scott Research Laboratories
Nitrogen dioxide (chamber)	(21.1)	115 ppm in N_2	GM	Matheson Gas Products
Nitrogen (Oxygen Free)	(-195.8)	99.998	Purge Gas	Matheson Gas Products

[1] Designated by supplier as a measure of purity; values in parentheses taken from *Handbook of Chemistry and Physics* (ref. 17).

[2] As designated by supplier.

[3] Injection mode: VL - Volatilization of liquid via heated injection manifold with N_2 purge gas (see Figure 6); L = Direct syringe injection of liquid into 125 liter Teflon bag; G = Direct syringe injection of gas into N_2-purged line or Teflon bag; GM = Injection of ppm level gas phase mixture via smog chamber injection system (see Figure 5).

[4] NS = Not specified by supplier.

[5] Dicyclopentadiene was "cracked" by distillation to give cyclopentadiene of b.p. 42.0° C; cyclopentadiene was injected.

Table 6. MEASUREMENT METHODS

MEASURED QUANTITY	METHOD	MANUFACTURER	RANGE	MDC[1]	STUDY[2]
O_3	Chemiluminescent	Bendix Model 8002	0-1 ppm	0.001 ppm	B,C
Oxidant	NBKI (Wet Bubbler)	—	0-1 ppm	0.001 ppm	C
NO	Chemiluminescent	TECO Model 14B	0-10 ppm	0.001 ppm	B,C
NO_2	Chemiluminescent	TECO Model 14B	0-10 ppm	0.001 ppm	B,C
NO_x	Chemiluminescent	TECO Model 14B	0-10 ppm	0.001 ppm	B,C
NO_2	Saltzman (Wet Bubbler)	—	0-5 ppm	0.005 ppm	C
SO_2	Pulsed Fluorescent	TECO Model 43	0-5 ppm	0.002 ppm	B,C
Individual HC	Gas Chromatography/ Flame Ionization	Perkin Elmer Model 900	>0.05 ppm (V/V)[5]	0.05 ppm (V/V)[5]	B,C
CH_2O	Chromotropic Acid (Wet Bubbler)	—	0-1 ppm	0.015 ppm	C
Solar Radiation[3]	Pyranometer	Eppley Model 2	0-2 Langleys	—	B,C
% Possible Minutes Sunshine[4]	—	—	—	—	B,C
Daily Maximum Temperature[4]	—	—	—	—	B,C

[1] Minimum detectable concentration.

[2] Identifies the study in which each measurement method was employed: bag studies are designated by "B", and chamber studies are designated by "C".

[3] Data collected by the U.S. Environmental Protection Agency, Division of Meteorology, Research Triangle Park, North Carolina.

[4] Data collected by U.S. Weather Service at the Raleigh-Durham Airport (ref. 18).

[5] This value is for direct injection of a 1 mℓ volume of sample.

Chamber Studies

Both instrumental and manual analytical techniques were employed in the chamber studies. Analytical O_3, NO, NO_2, and SO_2 data from automated instruments were recorded from each chamber for 10 minutes per hour. These data are reported in Appendix D as a single value for each chamber once per hour. The reported concentrations were reduced from strip chart recordings at times eight minutes into each 10-minute sampling period.

Oxidant, NO_2, and formaldehyde were determined by wet chemical techniques. Samples were collected twice daily from each chamber at 0900 and 1600 EST. Individual hydrocarbon concentrations were determined by gas chromatographic analyses of grab samples collected at 0500 and 1300 EST on the first day. Generally, by the second day the concentration of the compound of interest had been reduced to nondetectable levels (<0.05 ppm [V/V]). Therefore, hydrocarbon samples were not collected on the second and third days of a three-day run. Hydrocarbon analyses from chamber runs are reported in Appendix C.

Ozone--

Ozone was monitored with a Bendix Model 8002 Ozone Analyzer. The principle of this operation employs the chemiluminescent gas-phase reaction between ozone and ethylene. The instrument operates in the continuous mode with a range of 0 to 1 ppm and an MDC of 0.001 ppm. Calibration was performed using a stable ultraviolet light ozone generator. The output of the O_3 generator was determined by gas-phase titration of O_3 with known NO concentrations from certified standard mixtures of NO in nitrogen (ref. 19). A recent intercomparison of our NO calibration cylinder with four other certified calibration cylinders indicates the [NO] in our cylinder to be low by 6.5 percent. The reported ozone data have not been corrected, and a correction factor (multiplier) of 1.065 would be required to account for the above difference.

Oxidant--

For chamber studies, photochemical oxidant concentrations were measured by the NBKI technique (refs. 19,20). This involved passing a known volume of chamber air through two all-glass midget impingers in series; each contained a

1% neutral-buffered potassium iodide solution. These solutions were subsequently analyzed with a Bausch and Lomb Spectronic 100 spectrophotometer. Sampling times were usually 10 minutes at flow rates of 600 to 700 ml min^{-1}. Flow rate was controlled by a calibrated hypodermic needle protected from overspray by a dessicant cartridge and glass wool trap. The reported data have not been corrected for responses to sulfur dioxide, nitrogen dioxide, peroxyacyl nitrates or other oxidizing species. The equimolar negative interference by SO_2 is readily apparent in the first-day data from chamber runs with sulfur-containing species which produce considerable amounts of SO_2. In the reported data, the time assigned to a measurement of a chamber is the automated instrument sampling period for that chamber which is closest to the beginning of the bubbler sampling period.

Nitrogen Oxides (NO, NO_2, and NO_x)--

Nitrogen oxides were monitored with a TECO Model 14B NO-NO_x analyzer. The principle of operation employs the chemiluminescent gas-phase reaction between NO and O_3. Two modes of operation are required to determine both NO and NO_2. Nitric oxide is measured first using the reaction of NO and O_3. The determination of NO_2, however, requires catalytic reduction of NO_2 to NO prior to the reaction of NO with ozone. After reduction of NO_2 to NO, the signal from the total NO in the sample is taken to be the NO_x concentration. Electronic subtraction of the original NO signal from the NO_x signal gives the NO_2 concentration. The instrument operates in two intervals within a 90-second cycle corresponding to the two modes of operation: NO concentration is updated at the end on the first interval and NO_2 and NO_x concentrations are updated at the end of the next interval. The analyzer has a range of 0 to 10 ppm and an MDC of 0.001 ppm. Calibration of NO and NO_x was performed by dilution of a certified cylinder of NO in nitrogen. Calibration of NO_2 was performed by using the NO_2 produced from the gas-phase titration of known NO concentrations with O_3 from the calibrated ozone generator. As was noted in the earlier discussion of the ozone calibration procedure, the [NO] in our calibration cylinder was recently found to be 6.5 percent low. The reported NO, NO_2, and NO_x data have not been corrected, and a correction factor (multiplier) of 1.065 would be required to account for the above difference.

It has been demonstrated that nitric acid, PAN, and ethyl nitrate interfere with NO_2 and NO_x determinations in instruments of the type employed in this study (ref. 21). The interfering species were not determined in this study. Therefore, the reported NO_2 and NO_x data have not been corrected for interferences.

Nitrogen Dioxide--

In addition to the chemiluminescent measurements, the Saltzman method was used to determine nitrogen dioxide levels in the chambers (ref. 22). Chamber air was drawn through a glass, fritted Mae West bubbler containing Griess-Saltzman reagent. Sampling times were normally 15 minutes at flow rates of 600 to 800 ml min^{-1}. Flow rate was controlled by a calibrated hypodermic needle protected from overspray by a dessicant cartridge and glass wool trap. Samples were analyzed with a Bausch and Lomb Spectronic 100 spectrophotometer. The reported data have not been corrected for interferences from ozone or peroxyacyl nitrates. In the reported data, the time assigned to a measurement of a chamber is the automated instrument sampling period for that chamber which is closest to the beginning of the bubbler sampling period.

Sulfur Dioxide--

Sulfur dioxide was monitored with a TECO Model 43 Pulsed Fluorescent SO_2 Analyzer. The principle of operation employs the fluorescent decay of excited SO_2 molecules which have been energized by pulsed ultraviolet light (190-230 nm). The instrument operates in the continuous mode with a range of 0 to 5 ppm and an MDC of 0.002 ppm. Calibration was performed by the use of cylinders containing ppm levels of SO_2 in air. Cylinder concentrations were referenced to an NBS SO_2 permeation tube calibration system.

Specificity to SO_2 was demonstrated by the absence of response for unirradiated air mixtures of each of the following compounds: methanethiol, methyl sulfide, methyl disulfide, thiophene, carbonyl sulfide, and dimethyl sulfoxide. An absence of response was also noted for irradiated smog chamber mixtures of air, NO, NO_2, O_3, and either propylene, furan, or pyrrole.

Individual Hydrocarbons--

The concentrations of individual hydrocarbons in the bag and smog chamber studies were determined by gas chromatographic separation with flame ionization detection. A modified Perkin-Elmer Model 900 chromatograph was employed.

In the bag studies the 125-l Teflon bag reactors were brought into the laboratory for direct sampling. Ten-liter Teflon bags were used in the chamber studies to collect samples for subsequent hydrocarbon analyses. A Metal-Bellows MB-41 pump was employed to draw the sample from the Teflon bag through a 1-m long, 3.2-mm OD Teflon tube, into the gas sampling assembly of the GC, and through 1-ml sampling loop. After 30 seconds of sampling to insure adequate purging of the line and the sampling loop, the pump was turned off, and the 1-ml volume of sample was injected directly onto the analytical column with a gas sampling valve.

For analysis of most of the organic compounds except C_2 to C_5 hydrocarbons, separation was accomplished on a 60-m S.C.O.T. OV-101 column operating at 90° C. Flow rate of the helium carrier was 25 ml min^{-1}.

Separation of propylene and other C_2 and C_5 hydrocarbons was accomplished on a 1.8-m long, 3.2-mm OD stainless steel column packed with Durapak n-octane. The column temperature was 23° C, and the helium carrier flow rate was 12 ml min^{-1}.

A Hewlett-Packard Model HP-3352 data system acquired the output signal, integrated peak areas, and converted the areas into concentration values which were printed out by a teletype. Strip chart records of output signals were maintained to supplement data system records. A nominal MDC from the data system using a 1-ml direct injection was 0.05 ppm (V/V). Slightly lower concentrations could be observed from strip chart records. The effective MDC can be improved significantly to values lower than 0.1 ppb (V/V) by sample concentration techniques employing liquid oxygen trapping.

Identification and quantification of compounds was based on comparison of retention times and peak areas with those of calibration mixtures. Calibration was performed at three-week intervals and showed a precision of ±5 percent. Propylene and the other C_2 to C_5 hydrocarbon calibrations were performed using mixtures of each compound in air. These calibration mixtures were commercially supplied (Scott Research Laboratories) and certified to ±1 percent accuracy. Commercial calibration mixtures for the remaining compounds used in this study were not available. In view of this, the needed calibration mixtures were prepared at RTI by quantitative syringe injection of the pure compounds into Teflon bags containing 125-l of clean, dry air from the air supply.

Formaldehyde--

In the chamber studies, formaldehyde was determined by the chromotropic acid method (refs. 23,24). A 1% sodium bisulfite solution was employed as the collection medium. Chamber air was drawn through two glass midget impingers in series. Sampling times were normally 30 minutes, and flow rates ranged from 600 to 700 ml min^{-1}. Flow rate was controlled by a calibrated hypodermic needle which was protected from overspray by a dessicant cartridge and glass wool trap. Samples were analyzed with a Bausch and Lomb Spectronic 100 spectrophotometer after treatment with chromotropic and sulfuric acids. The reported data have not been corrected for interferences from ethylene, propylene, or other hydrocarbons. In the reported data, the time that has been assigned to a measurement of a chamber is the automatic instrument sampling period for that chamber which is closest to the beginning of the bubbler sampling period.

Solar Radiation--

Total solar radiation data reported in this study were collected by the U.S. Environmental Protection Agency Division of Meteorology. The solar radiometer, an Eppley Precision Spectral Pyranometer was located at a point approximately 0.5 km from the RTI Smog Chamber Facility. This instrument employs a thermopile sensing element and determines light intensity at wavelengths longer than 295 nm. The hourly average values reported in Appendix D were reduced from continuous strip chart records.

Environmental Variables--

Other environmental variables reported in this study (see Appendix D) are ambient air temperature at 3-hour intervals, the daily maximum temperature (T_{max}), and the percent of possible minutes of direct sunshine (% SS). The % SS is determined by a sunshine switch, which consists of two photoelectric cells and a recorder. One cell is shaded from direct sunlight; the other is not. These cells are connected such that the recorder is actuated when the intensity of direct sunshine is sufficient to produce a shadow. The temperature and the sunshine data are collected by the U.S. Weather Service (ref. 18) at the Raleigh-Durham Airport (RDU). RDU is located at a distance approximately 10 km from the RTI Campus.

PROCEDURE

The experimental program is summarized in Table 1. In addition to the static and dilution runs conducted in the smog chambers, six types of experiments were conducted in bag reactors. The procedures used in conducting the bag and chamber studies are described below.

Bag Studies

The six types of bag studies included ozone-forming studies at a high HC/NO_x ratio, ozone-forming studies at a low HC/NO_x ratio, dark stability tests of selected study compounds in air, light stability tests of selected study compounds in air, dark phase reactivity studies of selected compounds with ozone, and dark phase reactivity studies of selected compounds with NO_x.

Chemical analyses in these studies involved instrumental determination of the following species: O_3, NO_x, SO_2, and HC. In most of the experiments a 1-m long, 3.2-mm OD Teflon tube was used sequentially to allow direct sampling by each instrument. Midway through the experimental program in an effort to maintain continuous irradiation of the bag samples, a 5-m long 4.8-mm ID Teflon sampling tube was used to connect the instruments in the laboratory with bags located outdoors. This procedure was abandoned after implementation in favor of the original procedure of bringing bags into the laboratory for analysis. This measure was taken due to an apparent modification of NO_x levels by the longer sampling line.

During the battery of analyses, samples were drawn by each of the continuous analyzers (O_3, NO_x, and SO_x) for a duration of 3 to 4 minutes to allow adequate time for the signal to become stable. The concentrations were recorded on strip charts and also manually recorded from a DVM display. Sampling duration for hydrocarbon analysis was 30 seconds. Gas chromatographic data were recorded on strip charts, acquired and integrated by a data system, and printed out on a teletype.

Ozone-Forming Potential--

To evaluate the ozone-forming potential of each of the selected compounds, a reactivity screening test was devised and conducted. Mixtures of air, NO_x, and each selected compound were exposed to natural sunlight irradiation at ambient temperatures in 125-l Teflon bag reactors.

The decision to conduct a run was based on forecasts supplied by the National Weather Service Forecast Office at RDU. After the decision to conduct the experiment was made, each bag was filled with 25 liters of air from the air supply and then exhausted with a vacuum pump. This purging procedure was repeated. Each bag was then filled with 125 liters of clean, dry air by a timed fill from the air supply. Appropriate amounts of NO and NO_2 were added to each bag by timed injections. After storage in the dark for 15 minutes, nitrogen oxides were measured to allow comparison with the target initial conditions. Next, the test hydrocarbon compounds were introduced into the bags by syringe injection of the pure gas or liquid compound. The bags were then stored in the dark for 30 minutes to allow for volatilization and adequate mixing prior to initial NO, NO_2, and hydrocarbon analyses. Target initial conditions were 10 ppmC of the test compound and either 2.0 or 0.5 ppm NO_x (20% NO_2). Two NO_x levels were chosen to provide information at nominal initial HC/NO_x ratios of 5 and 20.

At the conclusion of the initial analyses, typically between 0900 and 1000 EST, the bags were taken more or less simultaneously outside and suspended from the bag support for exposure to sunlight. The irradiation period typically continued until 1600, except for the three or four brief interruptions required by chemical analyses. The duration inside the laboratory for O_3, NO, NO_2, and hydrocarbon analyses was kept to a minimum and ranged from 15 to 20 minutes for each battery of analyses.

Dark Stability--

Tests were conducted to evaluate the stability of air mixtures of selected test compounds in the dark. Results from these tests can be used to assess thermal decomposition, thermal oxidation, or dark phase surface-mediated effects contributed by the Teflon reactor walls.

The same 125-l Teflon bags that were employed in the ozone-formation screening test were used in this test. The procedure was similar to that used in the ozone-formation study. The bags were purged twice and then filled with clean, dry air from the air supply. The compounds of interest were introduced into the bags by syringe injection such that a concentration of 10 ppmC was achieved. To allow for volatilization and adequate mixing prior to initial hydrocarbon analyses, the bags were stored in the dark for 30 minutes. After the initial GC analyses, the bags were stored in the dark at room temperature and reanalyzed several times over an 8-hour period. Selected samples, however, were monitored periodically for longer periods, up to four days.

Light Stability--

Experiments were conducted to evaluate the stability of air mixtures of selected test compounds during and after exposure to natural irradiation.

Aside from the fact that NO_x was not injected, the procedure was the same as that employed in the ozone-formation study.

Dark Phase Reactivity with Ozone--

Tests were conducted to evaluate the dark phase reactivity of selected compounds with ozone. The same 125-l Teflon bags that were employed in the ozone-formation tests were used with this study. The bags were purged twice, and each bag was then filled with 125 liters of dry, ozonized, and otherwise clean air by a timed fill from the air supply. The initial ozone concentration of approximately 1.0 ppm was achieved by a timed activation of the ozone generator that had been installed in the line between the air supply and the bag. After storage in the dark for 30 minutes to allow for adequate mixing, ozone was measured. Next, selected test compounds were introduced into the bags by syringe injection to a concentration of 10 ppmC. After 30 minutes to allow for volatilization and adequate mixing, measurements of ozone and the test compound were conducted periodically for up to 6 hours.

Dark Phase Reactivity with NO_x--

Experiments were conducted to evaluate the dark phase reactivity of selected compounds with nitrogen oxides. Aside from the fact that during these tests the bags were stored in the dark at room temperature, the procedure was the same as that used for the ozone-formation study conducted at the lower HC/NO_x ratio. The target initial conditions were 10 ppmC of the test hydrocarbon and 2.0 ppm of NO_x (20% NO_2).

Smog Chamber Studies

Based on the results of the screening studies conducted in Teflon bags, six compounds were selected for three-day smog chamber experiments. These selected compounds are thiophene, pyrrole, furan, methanethiol, methyl sulfide, and methyl disulfide. The three-day experiments were conducted in the four-chamber RTI Smog Chamber Facility. Target initial conditions of 5 ppmC of the compound and 1 ppm of NO_x (20% NO_2) were employed. Three test compounds were studied simultaneously with one in each of the first three chambers. Propylene was employed in the fourth chamber as a control. Each of the selected compounds was subjected to experiments designed to simulate static and transport (dilution) atmospheric conditions.

Static Experiments--

A three-day smog chamber run requires four days of chamber activities. On the day before a run is to start the chambers are operated in the purge mode. Each chamber is flushed with ambient air at a flow rate of 2.0 m^3 min^{-1} starting at 0900 and lasting for six to eight hours. At approximately 1400 the purging operation is terminated, each chamber is sealed, and the cleanup operation is begun. Hydrocarbon and NO_x contaminants in the captive air parcel are removed by recirculation through the purification unit for 8 to 12 hours at a flow rate of 0.28 m^3 min^{-1}. The cleanup operation is terminated two hours prior to sunrise. For these experiments, the humidity of the captive air parcel was not altered during the cleanup. This was accomplished by "by-passing" both the humidifier and the desiccant columns during the cleanup operation.

The next step is pollutant injection. Appropriate amounts of NO and NO_2 were introduced sequentially into each chamber using the chamber injection system described earlier. After the NO_x injection, propylene was injected into the fourth chamber also using the injection system. Each of three different test compounds was then introduced into one of the three remaining chambers by syringe injection. The injection procedure was completed one hour before sunrise. This allowed 30 minutes for adequate mixing and 30 minutes for initial reactant sampling prior to sunrise.

The contents of the chambers were sampled and monitored for the next three days. Ozone, NO_x, and SO_2 were monitored once per hour for each chamber. Wet bubbler samples for oxidant, NO_2 and CH_2O analyses were typically collected from each chamber twice per day at 0900 and 1600 EST. Samples for hydrocarbon analyses were collected in 10-l Teflon bags at 0500 and 1300 EST on the first day. Generally, by the second day the concentration of the compound of interest had been reduced to nondetectable levels. Therefore, hydrocarbon samples were not collected on the second and third days. Generally, each three-day run was terminated at 1700 EST on the afternoon of the third day.

Dilution Experiments--

With one exception, the procedure emloyed in the dilution runs is the same as that described above for the static runs. The same target initial conditions were employed in both studies. After reactant injection had been completed, simulated dilution was initiated at 0800 EST on the first day. The chambers were operated in the dilution mode with a recirculation flow rate through the air purification system of 0.058 m^3 min^{-1}. Dilution was terminated after 24 hours of operation, and the chambers were operated under static conditions, similar to those described above, for the remaining two days of the three-day run. The dilution flow rate is such that after 24 hours of operation, 95 percent of an unreactive material originally present would be removed. The object of operation in the dilution mode is to simulate the dilution experienced by an air parcel as it is transported downwind.

SECTION 5

RESULTS AND DISCUSSION

CHOICE OF COMPOUNDS FOR STUDY

The 17 compounds chosen for examination in this study are listed in Table 1. These compounds were selected for several reasons. A primary objective was to select species which are expected to be released into the atmosphere by synthetic fuels processing operations. Potential emissions from such fuel conversion operations as coal gasification and liquefaction, shale oil production, and petroleum refining were identified from a literature survey (ref. 1). This report provided a basis for selecting many of the 17 compounds chosen for testing. Identified compounds with sulfur or nitrogen in their molecular structure, which had not been subjected to extensive smog chamber investigation, were given special consideration in the selection process. Other compounds, although not identified in the literature survey, were chosen because they were representative of a class of identified compounds or because of chemical or structural similarity to identified compounds. Emissions of a variety of saturated and unsaturated hydrocarbons are also anticipated. Considerable attention has been directed to elucidating the atmospheric chemistry of these compounds. For this reason, they are not considered in this study.

The sulfur-containing compounds, carbonyl sulfide, methanethiol, methyl sulfide, methyl disulfide, thiophene, and a substituted thiophene, 2-methylthiophene, were specifically identified in the literature survey and were chosen for testing. Other sulfur-containing species such as sulfur dioxide, hydrogen sulfide, and carbon disulfide were also identified. Examination of this latter group of compounds, however, is deferred to future studies.

Many of the nitrogen-containing species, which were identified as potential emissions, were found to include heterocyclic compounds such as pyrroles and pyridines. Pyrrole was chosen as the nitrogen-containing compound for study, leaving such species as ammonia, hydrogen cyanide, substituted pyrroles, and pyridines to future investigations.

Although furan was not identified in the literature review, it was chosen to complete a study of the five-membered heterocyclic class of compounds: sulfur-containing thiophene, nitrogen-containing pyrrole, and oxygen-containing furan. Two substituted furans, 2-methylfuran and 2,5-dimethylfuran, were chosen to examine the influence of added methyl groups on the ozone-forming potential.

Cyclopentadiene has been identified in coal gas, although it is not expected to be a major atmospheric emission. It was chosen because of its molecular structure. As a five-membered, all-carbon, cyclic molecule, its behavior can be compared with the five-membered heterocyclic compounds chosen for study.

The coal matrix is highly aromatic. Therefore, it is not surprising to find aromatic hydrocarbons identified as potential pollutants from fuel conversion operations. Toluene, ethylbenzene, and ortho-, meta-, and para-xylene were chosen for testing.

Although small amounts of propylene may be released from fuel conversion facilities, this compound is not expected to be a major emission. Propylene is the hydrocarbon that has been most frequently examined in smog chambers. For this reason, propylene was chosen as a control test compound.

BAG STUDIES

Several types of investigations were conducted in bags. A total of 106 bag experiments was performed. The first study was directed at assessing the ozone-forming potential of 16 compounds. Based on the results, six compounds were selected for additional bag and smog chamber experiments. The additional bag studies included dark stability tests of the selected compounds in air, light stability tests of the compounds in air, dark phase reactivity studies of the compounds with NO_x, and dark phase reactivity tests of the compounds with ozone. The raw data from these bag studies are compiled in Appendix B and are discussed in the following paragraphs. Results of the chamber studies are discussed in a subsequent subsection.

Ozone-Forming Potential

The reactivity of an organic material is the intrinsic ability of that compound to participate in atmospheric reactions which result in smog formation. Several attempts to quantify reactivity have been based on various manifestations of photochemical smog: hydrocarbon conversion, NO photooxidation rate, maximum O_3 concentration, O_3 formation rate, O_3 dosage, NO_2 dosage, formaldehyde yield, PAN yield, eye irritation index and others (ref. 25). The object of the screening tests presented here is to assess the reactivity of the test compounds on the basis of the maximum achieved O_3 concentration.

Previous studies (ref. 26) have shown the relationship between precursor concentrations and the resulting maximum ozone level to be highly nonlinear. This relationship may be represented in two dimensions by equal concentration lines (isopleths) of ozone maxima as a function of initial nitrogen oxides and initial hydrocarbon concentrations. This relationship may also be represented by a three-dimensional surface projection of ozone maxima as a function of initial nitrogen oxides and hydrocarbon concentrations. A hypothetical representation is presented in Figure 8. On this "ozone mountain" lies a ridge which defines the combinations of precursor concentrations required for maximum ozone production. The slope of this ridge of maximum ozone production may be represented by a HC/NO_x ratio.

The critical HC/NO_x ratio which defines the conditions for maximum ozone production is not the same for every organic molecule. The critical HC/NO_x ratio for propylene has been reported to be between 3 and 6 ppmC/ppm (ref. 27). Alkanes are considered to be less reactive than the olefin, propylene. For alkane-NO_x photochemical systems the HC/NO_x ratio which results in maximum ozone production ranges from 15 to 60 (refs. 4, 28, 29).

The objective of this study was not to identify the critical HC/NO_x ratio for each compound. Instead, it was to identify, for subsequent smog chamber testing, those compounds which can produce significant quantities of ozone. Toward this end, target initial conditions of 10 ppmC of the test compound and 2.0 and 0.5 ppm of NO_x were selected. These test conditions provide for initial HC/NO_x ratios of 5 and 20, which are expected to encompass regimes of potential ozone production ranging from that typical of propylene to that representative of an alkane hydrocarbon. Environmental variables, measured initial conditions, and selected results of the ozone-forming studies conducted at both low and high HC/NO_x ratios are summarized in Tables 7 and 8. If more details are desired, Appendixes A and B should

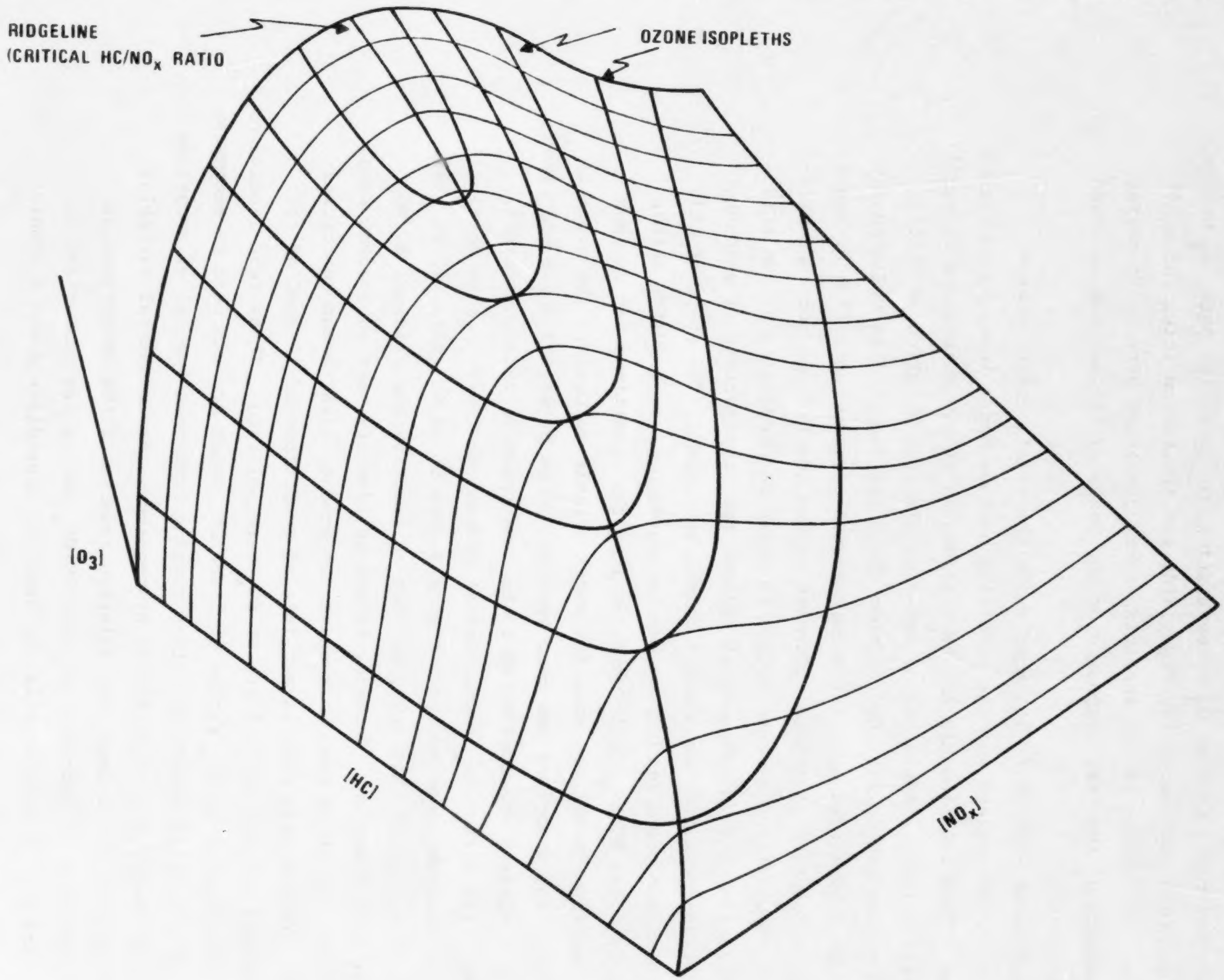
RIDGELINE
(CRITICAL HC/NO$_x$ RATIO
OZONE ISOPLETHS
[O$_3$]
[HC]
[NO$_x$]

Figure 8. Hypothetical representation of Ozone Maxima as a function of initial nitrogen oxides and hydrocarbon concentrations.

Table 7. SUMMARY OF SELECTED RESULTS OF OZONE-FORMING STUDIES CONDUCTED IN BAGS AT LOW INITIAL HC/NO_x RATIOS

		Environmental Variables			Initial Conditions					Results					
Compound	Date	T_{max}, °C	ΣSS^a	$\Sigma SR_{12}{}^b$	$[HC]i^c$	$[NO]i^d$	$[NO_2]i^d$	$[NO_x]i^d$	HC/NO_x	$X_{HC}{}^e$	$X_{NO_x}{}^f$	$\theta_{xo}{}^g$	$[O_3]^{d,h}_{max}$	$[SO_2]^{d,h}_{max}$	$X_{SO_2}{}^i$
Furan	6-10-76	33	28	226	10.1	1.154	0.264	1.418	7.1	1.00[j]	0.88	<66	1.066		
	6-2-76	29	32	150	9.62	1.370	0.310	1.680	5.7	1.00	0.83	<114	1.133		
Pyrrole	6-10-76	33	28	226	12.2	1.186	0.316	1.502	8.1	1.00	0.89	<104	0.627		
	6-9-76	33	40	144	11.4	1.700	0.282	1.982	5.8	1.00	0.84	<60	0.305		
Thiophene	6-10-76	33	28	226	10.1	1.108	0.274	1.382	7.3	0.58	0.58	88-175	0.256		
	6-29-76	33	66	152	9.48	1.570	0.462	2.032	4.7	0.66	0.92[k]	71-181	0.013	0.409	0.31
Methanethiol	7-1-76	29	55	170	8.71	1.696	0.492	2.188	4.0	0.85	0.83[k]	>270	0.0	0.928	0.13
Methyl sulfide	6-29-76	33	66	152	9.36	1.608	0.518	2.126	4.4	0.82	0.99[k]	<106	0.327	1.56	0.43
	7-1-76	29	55	170	10.2	1.684	0.456	2.140	4.8	0.91	0.99[k]	<78	0.261	0.926	0.20
Methyl disulfide	6-29-76	33	66	152	9.03	1.866	0.522	2.388	3.8	1.00	0.99[k]	<130	0.180	1.78	0.20
	7-1-76	29	55	170	12.1	1.960	0.496	2.456	4.9	1.00	0.98[k]	<90	0.212	2.13	0.18
Carbonyl sulfide	7-1-76	29	55	170	10.0[l]	1.712	0.512	2.224	4.5	—	0.88[k]	>285	0.0	0.045	0.005
Cyclopentadiene	7-16-76	35	71	110	10.7	1.606	0.720	2.326	4.6	0.80	0.77[k]	<122	1.596		
2-Methylfuran	6-10-76	33	28	226	10.8	1.134	0.264	1.398	7.7	1.00	0.58	<71	0.925		
2,5-Dimethylfuran	6-10-76	33	28	226	15.9	1.114	0.318	1.432	11.1	1.00	0.44	<113	0.841		
2-Methylthiophene	6-29-76	33	66	152	8.91[l]	1.570	0.473	2.043	4.4	1.00	0.97[k]	<83	0.333	0.766	0.53
Toluene	6-22-76	29	24	116	12.0	1.648	0.388	2.036	5.9	0.27	0.51[k]	>312	0.0		
Ethylbenzene	6-22-76	29	24	116	11.9	1.832	0.472	2.304	5.2	0.21	0.47[k]	>328	0.0		
O-Xylene	7-23-76	34	34	152	10.3	1.786	0.494	2.280	4.5	0.62	0.49[k]	81-285	0.385		
M-Xylene	7-23-76	34	34	152	10.4	1.920	0.530	2.450	4.2	0.62	0.58[k]	<94	1.008		
P-Xylene	7-23-76	34	34	152	10.1	1.814	0.552	2.366	4.3	0.14	0.05[k]	>333	0.0		
Propylene	8-19-76	27	92	283	8.55	1.318	0.320	1.638	5.2	0.98	0.52	<125	1.470		

[a] Percent possible minutes of direct sunshine measured at RDU Airport (ref. 18).

[b] Summation of solar radiation from beginning the exposure until 1200 EST; expressed in Langleys (cal cm^{-2}); measured by EPA; see text.

[c] Units = ppmC

[d] Units = ppm

[e] X_{HC} is the fractional conversion (loss) of hydrocarbons during the experiment; conversion of compound "a" at time t is defined as $X_a = ([\ ]_{initial} - [\ ]_t)/[\ ]_{initial}$.

[f] X_{NO_x} is the fractional conversion (loss) of NO_x during the experiment.

[g] Time to NO - NO_2 crossover, θ_{xo}, is expressed in minutes; the infrequent NO_x determinations in these bag studies prevent good resolution of this parameter.

[h] Represents maximum observed concentration, not necessarily maximum attained concentration.

[i] X_{SO_2} is the yield of SO_2 determined at $[SO_2]_{max}$ and is a measure of molecules of SO_2 formed per molecule of consumed sulfur.

[j] Based on estimated final concentration.

[k] Based on questionable concentration data.

[l] Initial HC concentration is calculated based on injected volume; no determinations were conducted.

TABLE 8. SUMMARY OF SELECTED RESULTS OF OZONE-FORMING STUDIES CONDUCTED IN BAGS AT HIGH INITIAL HC/NO$_x$ RATIOS

Compound	Date	Environmental Variables			Initial Conditions					Results					
		T_{max}, °C	ΣSS^a	ΣSR_{12}^b	$[HC]i^c$	$[NO]i^d$	$[NO_2]i^d$	$[NO_x]i^d$	HC/NO$_x$	X_{HC}^e	$X_{NO_x}^f$	θ_{xo}^g	$[O_3]_{max}^{d,h}$	$[SO_2]_{max}^{d,h}$	$X_{SO_2}^i$
Furan	6-2-76	29	32	150	10.4	0.370	0.075	0.445	23.4	0.95	0.74	<130	0.107		
Pyrrole	6-9-76	33	40	144	10.4	0.408	0.080	0.488	21.3	1.00	0.88	<30	0.385		
Thiophene	6-29-76	33	66	152	7.83	0.394	0.110	0.504	15.5	0.79	0.97^j	<58	0.060	0.426	0.29
Methanethiol	7-1-76	29	55	170	11.2	0.444	0.108	0.552	20.3	0.66	0.85^j	43-162	0.005	0.824	0.12
Methyl sulfide	6-29-76	33	66	152	10.7	0.392	0.128	0.520	20.6	0.49	0.97^j	<118	0.086	0.520	0.20
Methyl disulfide	6-29-76	33	66	152	11.0	0.404	0.094	0.498	22.1	1.00	0.97^j	<151	0.241	2.70	0.25
Carbonyl sulfide	7-1-76	29	55	170	10.0^k	0.430	0.128	0.558	17.9	—	0.86^j	>338	0.0	0.022	0.002
Cyclopentadiene	7-16-76	35	71	110	11.5	0.502	0.118	0.620	18.5	1.00	0.90^j	<135	0.622		
2-Methylfuran	6-10-76	33	28	226	10.8	0.292	0.062	0.354	30.5	0.97	0.46	<76	0.088		
2,5-Dimethylfuran	6-10-76	33	28	226	10.4	0.290	0.062	0.352	29.6	1.00	0.19	<117	0.297		
2-Methylthiophene	6-29-76	33	66	152	12.0	0.506	0.154	0.660	18.2	0.90	0.96^j	<94	0.038	0.591	0.29
Toluene	6-22-76	29	24	116	11.2	0.376	0.096	0.472	23.7	0.36	0.87^j	<89	0.343		
Ethylbenzene	6-22-76	29	24	116	11.4	0.462	0.172	0.634	18.0	0.51	0.87^j	~ 99	0.313		
O-Xylene	7-23-76	34	34	152	9.9	0.438	0.112	0.550	18.0	0.60	0.61^j	<75	0.521		
M-Xylene	7-23-76	34	34	152	10.1	0.466	0.126	0.592	17.1	0.80	0.61^j	<88	0.569		
P-Xylene	7-23-76	34	34	152	9.9	0.472	0.124	0.596	16.6	0.48	0.53^j	<98	0.594		
Propylene	8-19-76	27	92	283	9.0	0.318	0.074	0.392	23.0	0.82	0.45	<130	0.289		

[a] Percent possible minutes of direct sunshine measured at RDU Airport (ref. 18).

[b] Summation of solar radiation from beginning the exposure until 1200 EST; expressed in Langleys (cal cm^{-2}); measured by EPA; see text.

[c] Units = ppmC

[d] Units = ppm

[e] X_{HC} is the fractional conversion (loss) of hydrocarbons during the experiment; conversion of compound "a" at time t is defined as $X_a = ([\ ]_{initial} - [\ ]_t)/[\ ]_{initial}$

[f] X_{NO_x} is the fractional conversion (loss) of NO$_x$ during the experiment.

[g] Time to NO - NO$_2$ crossover, θ_{xo}, is expressed in minutes; the infrequent NO$_x$ determinations in these bag studies prevent good resolution of this parameter.

[h] Represents maximum observed concentration, not necessarily maximum attained concentration.

[i] X_{SO_2} is the yield of SO$_2$ determined at $[SO_2]_{max}$ and is a measure of molecules of SO$_2$ formed per molecule of consumed sulfur.

[j] Based on questionable concentration data.

[k] Initial HC concentration is calculated based on injected volume; no determinations were conducted.

be consulted. Appendix A is a summary of environmental conditions for each day of bag and chamber experiments. Appendix B provides a chronological tabulation of all the concentration-time data collected in the bag studies.

Examination of Tables 7 and 8 reveals that the oxidant standard, 0.08 ppm, was exceeded in at least one of the two test conditions for every test compound except carbonyl sulfide and methanethiol. Although methanethiol produced only small quantities of ozone, significant quantities of SO_2 were produced.

Ratios of maximum ozone levels achieved by the test compound to that produced by propylene are compared at both HC/NO_x ratios in Table 9. At the low HC/NO_x ratio, propylene produced 1.470 ppm of ozone. Only cyclopentadiene produced more ozone than propylene. Four hydrocarbons--the three furans and m-xylene--produced more than 50 percent of the amount generated by propylene. During the 300-minute exposure to natural irradiation only five of the test compounds failed to achieve $NO-NO_2$ crossover and therefore also failed to produce ozone. Nevertheless, this does not eliminate the possibility of ozone generation for multiple-day exposures.

At the high HC/NO_x ratio, propylene produced 0.289 ppm ozone. Eight compounds produced more ozone than propylene for this test condition. The three xylenes and cyclopentadiene produced approximately twice this amount. Pyrrole, methyl disulfide, 2,5-dimethylfuran, toluene, and ethylbenzene produced only slightly more ozone than did propylene.

The ratios of the ozone maxima observed at the low HC/NO_x condition to that at the high value are also presented in Table 9. The value for propylene is 5.09. It may be postulated that compounds with similar values may have reactivities similar to propylene, while compounds with lower values have reactivities more typical of alkane hydrocarbons. Certainly additional experiments at other HC/NO_x ratios are required to obtain an ozone response surface for each compound, which would allow this hypothesis to be tested.

Substituted Methyl Groups--

The influence of substituted methyl groups on ozone production may be examined by comparing the behavior of the three furans, the two thiophenes, the thiol and sulfide, and the aromatics.

Table 9. COMPARISON OF MAXIMUM OZONE CONCENTRATIONS ACHIEVED IN BAGS AT LOW AND HIGH HC/NO_x RATIOS

Compound	R_{LOW}[a]	R_{HIGH}[b]	$O_{3,L}/O_{3,H}$[c]
Furan	0.73, 0.77	0.37	10.6[d]
Pyrrole	0.43, 0.21	1.33	0.79[d]
Thiophene	0.17, 0.009	0.21	0.22[d]
Methanethiol	0.0	0.02	0.0
Methyl sulfide	0.22, 0.18	0.30	3.80[d]
Methyl disulfide	0.12, 0.14	0.83	0.75[d]
Carbonyl sulfide	0.0	0.0	--
Cyclopentadiene	1.09	2.15	2.57
2-Methylfuran	0.63	0.30	10.5
2,5-Dimethylfuran	0.57	1.03	2.83
2-Methylthiophene	0.23	0.13	8.76
Toluene	0.0	1.19	0.0
Ethylbenzene	0.0	1.08	0.0
O-Xylene	0.26	1.80	0.74
M-Xylene	0.69	1.97	1.77
P-Xylene	0.0	2.06	0.0
Propylene	1.00	1.00	5.09

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[a] Ratio of $[O_3]_{max}$ for specified compound to $[O_3]_{max}$ for propylene at low HC/NO_x ratio; see Table 7 .

[b] Ratio of $[O_3]_{max}$ for specified compound to $[O_3]_{max}$ for propylene at high HC/NO_x ratio; see Table 8 .

[c] Ratio of $[O_3]_{max}$ at low HC/NO_x to $[O_3]_{max}$ at high HC/NO_x for specified compound; see Tables 7 and 8 .

[d] In those cases where two runs were conducted at the low HC/NO_x condition, the tabulated ratios were calculated using same day results.

At the low HC/NO_x ratio for the furans, less ozone is produced with the addition of methyl groups. At the higher HC/NO_x ratio the reverse situation occurs. This suggests that the addition of methyl groups to furan reduces the critical HC/NO_x ratio.

Although data for the thiophenes are more scattered, these results also suggest that the conditions for maximum ozone production occur at a lower HC/NO_x ratio for 2-methylthiophene than for the unsubstituted molecule. The data do not allow speculation on the location of the critical HC/NO_x ratio for methanethiol or methyl sulfide. Comparison of ozone maxima for these two species also suggests increased ozone generation with substitution.

Five aromatic hydrocarbons were examined: toluene, ethylbenzene, and o, m, and p-xylene. Toluene and ethylbenzene exhibited similar behavior and produced the least ozone of the examined aromatics. Both species failed to produce ozone at the low HC/NO_x ratio while producing in excess of 0.3 ppm at the higher ratio. This suggests that the critical HC/NO_x ratio for these compounds is greater than 5 and may be in the range of 10 to 30. The xylenes exhibit similar behavior at the high HC/NO_x ratio forming almost twice the ozone produced by either toluene or ethylbenzene at these conditions. At the low HC/NO_x ratio, ozone production by each of the xylenes is dramatically different. Meta-xylene produced over 1.0 ppm ozone, para-xylene produced no ozone, and ortho-xylene produced an intermediate amount. From this behavior it may be speculated that the critical HC/NO_x ratio is low for m-xylene and may be around 5. The analogous value for para-xylene should be in the range of 10 to 30. The ortho-xylene may have a critical HC/NO_x value intermediate between the values for the meta and para isomers.

The trends of ozone production reported for the aromatic hydrocarbons in this study are generally consistent with results observed in other smog chamber studies (refs. 25, 30, 31). Substitution of a methyl group on a ring carbon of the toluene molecule has a considerable impact on the ozone-generative capacity of the molecule. Lengthening the side chain has little effect as is seen by comparing experiments conducted with toluene and ethylbenzene. Addition of a methyl group to a ring carbon of toluene forms a xylene and significantly increases the ozone-generative capacity of the molecule--almost doubling the maximum ozone at the high HC/NO_x ratio. Among the xylenes at the low HC/NO_x conditions, the meta isomer produces significantly more ozone than the other two isomers. The consumption of m-xylene is also the highest of the tested aromatic hydrocarbons.

The hydroxyl radical is believed to be the primary reactive species in photochemical smog reactions. Rate constants for HO attack on toluene, ethylbenzene, p-xylene, o-xylene, and m-xylene are 8.8×10^3, 11.8×10^3, 18.3×10^3, 20.6×10^3, and 34.6×10^3 ppm^{-1} min^{-1} (ref. 32). Comparison of the relative magnitudes of these rate constants for the aromatic hydrocarbons is generally consistent with ozone production observed at the low HC/NO_x ratio in this study. For the xylenes which exhibit dramatically different behavior at the low HC/NO_x ratio, the rate constant for the reaction of hydroxyl radicals with m-xylene is approximately 80 percent larger than the values for o- or p-xylene.

Heterocyclics--

Three five-membered heterocyclic compounds having cis-diene structures were examined: furan, pyrrole, and thiophene. At the low HC/NO_x ratio, furan formed the most ozone followed by pyrrole and thiophene. The five-member all-carbon cyclic cis-diene compound, cyclopentadiene, formed more ozone than any of the heterocyclics. In fact, among all the compounds tested, cyclopentadiene formed the most ozone. The increased ozone-generative capacity may be attributed to the molecular structure of the diene. Cycloolefins have been found to be among the most reactive of olefinic hydrocarbons (ref. 33).

During each experiment a fraction of the NO_x was converted to species nondetectable by the chemiluminescent NO_x analyzer. At the conclusion of a run with the heterocycles, up to 90 percent of the NO_x was unaccounted for. This is almost double the value for propylene. This may also suggest the generation of increased levels of NO_x-scavenging radicals for the heterocyclics as compared to propylene.

Among the heterocyclics, thiophene was the slowest reacting species. At the low HC/NO_x ratio, thiophene required approximately twice as much irradiation time as either furan or pyrrole to achieve $NO-NO_2$ crossover. At each HC/NO_x ratio, hydrocarbon consumption was near 100 percent for pyrrole and furan, while thiophene consumption ranged from 58 to 79 percent. This suggests that thiophene may have the potential for ozone production, which could extend for several days.

In addition to the ozone formed by the photooxidation of thiophene, sulfur dioxide was also observed as a product. Maximum SO_2 concentrations in excess of 0.4 ppm were achieved. The maximum yields of SO_2 (molecules of SO_2 formed per molecule of consumed sulfur at the time of the maximum $[SO_2]$) were approximately 0.30. These values were observed with concurrent ozone maxima below 0.1 ppm. For 2-methylthiophene at the low HC/NO_x ratio, a maximum SO_2 yield of 0.53 was observed concurrently with 0.33 ppm ozone. This suggests that for thiophenes, combinations of initial conditions which give rise to increased ozone generation may also enhance SO_2 production.

Sulfur-Containing Compounds--

Six sulfur-containing species were examined: methanethiol, methyl sulfide, methyl disulfide, carbonyl sulfide, thiophene, and 2-methylthiophene. Two of these compounds, methanethiol and carbonyl sulfide, failed to generate ozone at either HC/NO_x ratio. In contrast, methyl sulfide, methyl disulfide, thiophene, and 2-methylthiophene, were observed to produce ozone at both HC/NO_x ratios. Ozone production for thiophene in comparison to the sulfides appears to be more sensitive to initial HC/NO_x ratio.

Although the data do not allow clear resolution, methyl disulfide may have the largest ozone-generative capacity of the tested sulfur-containing compounds. Based on measured hydrocarbon consumption, methyl disulfide and 2-methylthiophene are the most reactive of the tested sulfur species. Hydrocarbon consumption for both compounds was 100 percent at the low HC/NO_x ratio, whereas consumption of the other species ranged from 58 to 91 percent.

Sulfur dioxide was observed as a product of the photooxidation of each of the sulfur-containing compounds. This is contrary to the finding of Cox and Sandalls (ref. 34) who failed to detect SO_2 during photooxidation experiments with methyl sulfide. This discrepancy may be attributed to the reduced light intensity employed in their study. The k_1 value (ϕk_a for NO_2) used in their study was 3.1×10^{-2} min^{-1}; this is approximately 10 percent of the accepted noontime value of 50×10^{-2} min^{-1}.

In most cases, the maximum SO_2 yields observed for each species were relatively insensitive to changing HC/NO_x ratio. Carbonyl sulfide produced the least SO_2, 20 to 50 ppb. Methanethiol produced levels of SO_2 slightly less than 1.0 ppm and had maximum yields of 0.13 and 0.12. Methyl disulfide produced the largest observed concentration of SO_2, 2.7 ppm. Both methyl sulfide and methyl disulfide produced SO_2 yields of approximately 0.20. The largest SO_2 yields were observed for thiophene and 2-methylthiophene with values ranging from 0.29 to 0.53.

Selection of Compounds for Subsequent Bag and Chamber Studies--

Three families of compounds were examined in screening tests: aromatics, heterocyclics, and open-chain sulfur species. The results of the screening tests have shown that in the photooxidation of 14 of the 16 test compounds, ozone in excess of the NAAQS was produced. Although photooxidation of methanethiol produced no ozone, substantial amounts of SO_2 were formed. Among the test compounds, the aromatic hydrocarbons have received considerable smog chamber investigation (refs. 25, 30, 31). This leaves two families of compounds for additional bag and smog chamber investigations: the heterocyclics and the sulfides. Three compounds were chosen from each category. The unsubstituted (parent) heterocyclic molecules, furan, pyrrole, and thiophene, were selected from the first group. The sulfur-containing compounds, methanethiol, methyl sulfide, and methyl disulfide, were chosen from the second category. As in the screening tests, propylene was chosen as a control test compound for many of the bag and chamber experiments.

Dark Stability

The stability of each of the six selected compounds was evaluated in the dark at room temperature. A nominal concentration of 10 ppmC in air was employed. Results from this study are summarized in Table 10. Rate constants for assumed first order decays and the corresponding coefficients of determination, r^2, were calculated. Half-lives were calculated in the usual manner for first order reactions by dividing ln 2 by the rate constant.

Stability tests were conducted over periods ranging from 3 to 6 days for the heterocyclic species. These compounds are highly stable in the dark with half-lives in excess of 300 hours and loss rates ranging from 8 to 25

Table 10. SUMMARY OF DARK STABILITY RESULTS

Compound	Date	Initial Concentration ppmC	Test Duration, hr	Mean Concentration (±1SD) ppmC	Number of Measurements	k[1] hr^{-1}	r^2[2]	Half-life,[3] hr
Furan	5-25-76	10.8	71	10.31 ± 0.52	8	1.64×10^{-3}	0.77	420
Thiophene	5-26-76	9.8	144	9.68 ± 0.39	7	0.78×10^{-3}	0.79	880
Pyrrole	5-27-76	11.2	114	10.00 ± 1.09	4	2.07×10^{-3}	0.92	330
CH_3SH	8-5-76	8.16	6.0	9.13 ± 0.69	5	[4]	—	[4]
CH_3SCH_3	8-5-76	11.4	4.7	11.15 ± 0.35	2	9.60×10^{-3}[5]	—	72[5]
$(CH_3S)_2$	8-5-76	12.3	4.7	12.05 ± 0.35	2	8.89×10^{-3}[5]	—	78[5]

[1] Rate constant for an assumed first order decay.

[2] Coefficient of determination for a least squares fit of ℓn C vs t

[3] Half-life = ℓn 2/rate constant

[4] The variability of the methanethiol determinations masked any trend in behavior.

[5] These values may be questionable because they are based on only two determinations.

ppb hr^{-1}. Among the tested heterocycles, pyrrole is the least stable and thiophene is the most stable.

The stability tests for methanethiol, methyl sulfide, and methyl disulfide were conducted over periods of 5 to 6 hours. This is slightly less than the duration of a typical one-day ozone-forming irradiation. These compounds exhibited moderate stability over the test periods. No loss rate could be calculated for methanethiol because the variability of the measured values over the 6-hour test masked any trends. Although a loss is indicated for the sulfide and disulfide, two determinations are considered to be too few to yield reliable results.

Methyl disulfide and methanethiol have been reported in the literature to be relatively stable in the dark. At concentrations of less than 0.5 ppm of the disulfide, a 1-day loss rate in Teflon bags of 0.4 percent hr^{-1} has been reported (ref. 35). This value is consistent with the value in Table 10. Methanethiol at 1,000 ppm was reported to decay by only 10 percent over a 9-day period (ref. 36). This reported stability may not be indicative of the stability of the compound at the lower concentrations used in our study.

These results suggest that air mixtures of all six test compounds are relatively stable in the dark. The methanethiol concentration may have been influenced by interactions with the Teflon walls of the bag reactor or other unknown phenomena, which could give rise to the observed erratic behavior. The other five species exhibited no behavior in these experiments, which would suggest the occurrence of spontaneous or surface-mediated decomposition or oxidation processes. Additional experiments may be necessary to provide better definition of the long-term behavior of methanethiol, methyl sulfide, and methyl disulfide in the dark.

Light Stability

The stability of five of the six test compounds was evaluated during single-day irradiations at a nominal initial concentration of 10 ppmC in air. A leaking bag prevented the completion of the experiment with methanethiol. The duration of each experiment was approximately 6 hours. Concentration-time data were fitted to the form of a first order decay. Each rate constant with its coefficient of determination, r^2, was calculated. The half-life of each test species was determined in the usual manner under the assumption of first order reactions.

Except for methyl sulfide, the introduction of sunlight enhanced the decay rates of the tested species in comparison to the rates observed in the dark. The ratio of the dark to the light half-lives can serve as a parameter for comparing decay rates. Using this approach and the half-lives in Tables 10 and 11, furan is seen to decay approximately 6 times faster under natural irradiation than in the dark. For thiophene, pyrrole, and methyl disulfide the effects of sunlight are even more pronounced: increasing the decay rates by over 20-fold.

On an absolute basis, only pyrrole and methyl disulfide were observed to have half-lives of less than 1 day. This suggests that in the atmosphere in the absence of NO_x-mediated photooxidation, pyrrole and methyl disulfide are removed relatively quickly. Product information is not available for the heterocycles; however, sulfur dioxide was measured as a decay product of the sulfides. The highly stable methyl sulfide has a half-life of 57 hours and produced only 44 ppb of SO_2. In contrast, methyl disulfide, with a half-life of only 3 hours, produced significant quantities of SO_2: a maximum SO_2 concentration of 2.4 ppm was observed. This corresponds to an SO_2 yield of 0.28 which is slightly higher than the yields observed in the ozone-forming studies discussed earlier.

Rayner and Murray (ref. 36) conducted irradiations of methanethiol, methyl sulfide, and methyl disulfide at concentrations of 1,000 ppm in air. These studies were conducted with artificial irradiation at 360 nm. Under the 360 nm light, methyl sulfide was stable, decaying by only 3.5 percent after 9 days of exposure. In addition, methanethiol was exposed to natural sunlight. Methanethiol decayed at approximately equal rates under artificial and natural irradiation, decaying by 68 percent and 65 percent after 9 days. Methyl disulfide was the least stable of the three compounds and exhibited a 91 percent loss after 9 days.

The results of the Rayner and Murray study at high concentrations are qualitatively consistent with the results for methyl sulfide and methyl disulfide presented in Table 11. If the referenced findings may be extrapolated to the low concentration behavior of methanethiol, then a half-life between 3 and 57 hours (perhaps 10 hours) is anticipated at 10 ppmC (the conditions shown in Table 11).

The reason for the increased decay rates under exposure to natural irradiation is not apparent. It may be theorized that the enhanced decay

Table 11. SUMMARY OF LIGHT STABILITY RESULTS

Compound	Date	Initial Concentration, ppmC	Test Duration, hr	Number of Measurements	k[1], hr^{-1}	r^2[2]	Half-Life,[3] hr
Furan	6-2-76	9.0	5.7	4	1.06×10^{-2}	0.90	65
Thiophene	6-8-76	10.1	5.7	5	1.65×10^{-2}	0.92	42
Pyrrole	6-9-76	11.1	5.4	5	4.62×10^{-2}	0.95	15
CH_3SCH_3	7-1-76	11.1	5.3	4	1.22×10^{-2}	0.87	57
$(CH_3S)_2$	7-1-76	12.0	1.9	4	21.9×10^{-2}	1.00	3.2

[1] Rate constant for an assumed first order decay.

[2] Coefficient of determination for the least squares fit of $\ln C$ vs t.

[3] Half-life = $\ln 2$/rate constant.

rates are due to photolysis of the tested species. Published UV absorption spectra suggest that furan, pyrrole, thiophene, and methyl sulfide do not absorb at 290 nm (refs. 37, 38). Methyl disulfide was found to absorb at 290 nm (ϵ = 60), and methanethiol was found to absorb weakly at 280 nm (ϵ = 20) (ref. 38). The symbol ϵ (1 mole^{-1} cm^{-1}) represents the decadic form of the molar extinction coefficient. Bond energy considerations for these two species have shown photodissociation to be theoretically possible in natural sunlight. Absorption and photolysis data which could be employed to confirm and perhaps quantify the behavior of these two species were not found in the literature.

An alternate explanation for the increased decay rates on exposure to natural sunlight may involve destructive secondary reactions following photoexcitation. Wood and Heicklen (ref. 39) have suggested that this mechanism accounts for the photooxidation of CS_2 at 313 nm, whereas wavelengths below 230 nm are required for direct photodissociation. This may also occur for compounds in our study.

A third explanation for the enhanced decay rates may be the so-called "dirty-chamber" effect. It has been suggested that irradiation chambers exhibit this effect in the form of a wall source of HO radicals (ref. 40). If this is the case, then a chain reaction initiated by HO radicals may be required to explain the data. This hypothesis may be questioned, however, considering that the rate of methyl sulfide decay was unaffected by irradiation.

Dark Phase Reactivity with Ozone

Experiments were performed to determine the reactivity of ozone in the dark with each of the six test compounds. Propylene was also tested as a reference compound. These tests were conducted in the batch mode in 125-l Teflon bag reactors. The duration of each test was dependent on the reactivity of the test compound and was generally between 2.0 and 8.0 hours. During each test, both HC and O_3 determinations were performed. Target initial concentrations were chosen to maintain an excess of hydrocarbon and simplify data treatment.

A summary of the results of these tests is presented in Table 12. Ozone concentration-time data were fitted to the form of a first-order decay. The resulting uncorrected rate constants and corresponding coefficients

Table 12. SUMMARY OF RESULTS OF DARK REACTIVITY EXPERIMENTS WITH OZONE

Compound	Date	$[O_3]_{Initial}$ ppm	$[HC]_{Initial}$ ppmV	k[1] hr^{-1}	r^2[2]	k[3] hr^{-1}	$\overline{[HC]}$[4] ppmV	k[5] $ppm^{-1}hr^{-1}$	Half-Life[6] hr
Furan	6-2-76 2-4-77	0.77 0.31	0.57 3.93[7]	0.158 0.625	0.98 1.00	0.149 0.616	0.485 3.72	0.307 0.166	2.3 4.2
Thiophene	6-3-76 2-4-77	0.85 0.71	1.23 4.49	0.0225 0.220	0.96 0.99	0.0136 0.212	1.14 4.44	0.0119 0.0477	58 15
Pyrrole	6-3-76 2-4-77	0.88 0.24[7]	— 2.25	0.548 2.81	0.98 0.99	0.539 2.80	0.625[7] 1.97	0.862 1.42	1.2 0.49
CH_3SH	8-5-76	1.10	7.71	0.0465	1.00	0.0376	7.71	0.00488	140
CH_3SCH_3	8-5-76	0.90	4.87	0.0573	0.99	0.0484	4.87	0.00994	70
$(CH_3S)_2$	8-5-76	1.12	6.37	0.0254	1.00	0.0165	6.37	0.00259	270
Propylene	2-4-77	0.23	1.60	1.48	1.00	1.47	1.44	1.02	0.68

[1] Pseudo-first order rate constant based on O_3 concentration-time data; these values are uncorrected for dark phase O_3 decay in the Teflon bag reactors.

[2] Coefficient of determination for a least squares fit of $\ell n[O_3]$ vs t.

[3] Pseudo-first order rate constant corrected for dark O_3 decay measured in the bags ($k_{O_3,dark}$ = $8.86 \times 10^{-3}\ hr^{-1}$).

[4] Mean HC concentration over the duration of the test.

[5] Second order rate constant for reaction between the test compound and ozone.

[6] Half-life is tabulated for either compound, assuming a constant concentration 1 ppmV for the other; this assumes a stoichiometry of 1:1 and may not be valid for the sulfur-containing compounds (see text.

[7] Estimated concentrations.

of determination for the first order fits are tabulated. Each uncorrected pseudo-first order rate constant is then corrected for dark phase decay of ozone within the bag. This value is divided by the mean concentration of the test compound for the experiment, yielding the approximate second order rate constant. A half-life for one reactant (either HC or O_3) is then calculated based on an assumed constant concentration of 1 ppm for the second reactant.

The tabulated second order rate constants are based on only one or two experiments and should therefore be considered as approximate values. The r^2 values for these determinations were generally better than 0.95, suggesting good agreement between the concentration-time data and the assumed model. In addition, the agreement between the experimentally determined rate constant for propylene, 1.02 ppm^{-1} hr^{-1}, and the established value, 0.954 ppm^{-1} hr^{-1} (ref. 11), increases confidence in the quality of the data.

Two rate constant determinations were performed for each of the heterocycles. The initial reactant concentrations differed substantially for the two determinations. This difference may account for the discrepancies between the rate constants determined for these two conditions.

Reaction stoichiometries could be determined with confidence for only furan and propylene. In the two furan experiments 1.1 and 0.8 molecules of ozone were required to remove 1 molecule of furan, while propylene required 0.7. These values are in line with the generally accepted value of 1.0 for propylene (ref. 41). The concentration behavior of the remaining five compounds during the experiments did not allow an accurate assessment of their stoichiometries. Qualitative evaluation of this data indicates that the $\Delta O_3/\Delta HC$ ratios for the aliphatic sulfides are greater than 1.0. This is consistent with the values of 1.8 and 3.9 reported for the reaction of ozone and methanethiol and ozone and methyl disulfide in aqueous solution (ref. 42).

The literature is generally lacking in gas phase ozonolysis studies of the test compounds. Palmer (ref. 37) suggested from solution-phase studies that ozone electrophilically attacks the 2- and 5-positions of the five-membered heterocyclic molecule. The anionic oxygen atom of the intermediate then attacks the 3- or 5-positions. Decomposition of the resulting molecules may yield glyoxals, keto aldehydes, and other oxygenates.

Although product identification was not attempted in our study, gas phase ozonolysis of alkyl sulfides at high ozone concentrations (>1%) have been reported to yield both the sulfoxide and the sulfone (ref. 42). Cox and Sandalls (ref. 34) have reported that methyl sulfide is unreactive with ozone (at 2.8 ppm) in the dark. It is likely that the heterogeneous component contributing to ozone decay in their experimental system was sufficient to mask any contribution to ozone decay by reaction with methyl sulfide. This is consistent with the small rate constant presented in Table 12.

The ozonolysis of ethanethiol was studied by Kirchner et al. (ref. 43). The reaction was found to proceed by carbon-sulfur bond cleavage, and a rate constant of 0.35 ppm^{-1} hr^{-1} was reported. This is approximately 73-fold larger than our finding of 0.0049 ppm^{-1} hr^{-1} for the homologue, methanethiol. The strength of the C-S bond is 2.5 kcal larger for methanethiol than ethanethiol. This would suggest a reduced rate constant for methanethiol, although the reduction is difficult to quantify. Initial reactant concentrations used by Kirchner were an order of magnitude larger than were employed in our study. This may also contribute to the above differences in ozonolysis rate constants.

The results in Table 12 indicate that among the six test compounds, pyrrole and furan react most rapidly with ozone. The reactivity of pyrrole is very similar to that of the reactive olefin, propylene. In contrast, the sulfur-containing species are considerably less reactive. Among the tested sulfur compounds, the heterocycle, thiophene, is the most reactive with ozone. Reactivity among the open chain sulfur species decreases from methyl sulfide to methanethiol to methyl disulfide. These relative reactivities are somewhat speculative due to the approximate nature of tabulated rate constants. The concentration of each of these compounds remained essentially unchanged over the 5 to 6 hours required for the ozone reactivity experiments. This, in addition to the results in Table 12, suggests that the tested open-chain sulfur species are not highly reactive with ozone.

Dark Phase Reactivity with NO_x

Tests were conducted to evaluate the dark phase reactivity of nitrogen oxides and each of the test compounds. In addition to the six test compounds, carbonyl sulfide (COS) was also chosen for testing. In the ozone formation tests conducted earlier, irradiated mixtures of COS and NO_x exhibited peculiar behavior. Although $NO-NO_2$ crossover was not achieved, and no ozone was formed, NO_x was consumed quickly at both HC/NO_x ratios. Carbonyl sulfide was therefore chosen for dark phase reactivity tests with NO_x to investigate this phenomenon. Furan, thiophene, and pyrrole were monitored in the presence of NO_2. Methanethiol, methyl sulfide, methyl disulfide, and carbonyl sulfide were tested in the presence of NO_x (a mixture of 80% NO and 20% NO_2). In addition, control experiments were conducted with air-NO_2 mixtures and air-NO_x mixtures. Results of these experiments are summarized in Table 13.

Mean hydrocarbon concentrations for each experiment are presented in the second major column of Table 13, and if decay was observed with time, a first-order decay constant is tabulated. Concurrent NO_x behavior is displayed in the third column as a first-order decay constant. In the fourth major column, the concurrent behavior of NO in the presence (and absence) of hydrocarbons is tabulated as the ratio of the experimentally determined second order NO oxidation rate constant to the established value (ref. 11).

The dark phase stability of furan, thiophene, and pyrrole was examined in the presence of NO_2. The thiophene and pyrrole decay rates exceeded those observed in the dark stability tests conducted in the absence of NO_2 (see Table 10). The largest increase, a factor of 10, was observed for pyrrole; whereas increases of approximately 3 were observed for thiophene. In these tests, NO_2 behavior in the presence of either thiophene or pyrrole was similar to that observed in the absence of hydrocarbons (control). The decay rate of NO_2 in the presence of furan, however, was increased by over threefold in comparison to that of the control.

It should be noted that these results are based on single experiments and may not be totally valid. The results do suggest, however, that in the dark, furan, thiophene, and pyrrole are relatively unreactive with NO_2 in comparison to their behavior with NO_x under irradiation.

Dark phase stability tests in the presence of NO_x were conducted with methanethiol, methyl sulfide, methyl disulfide, and carbonyl sulfide. Among these compounds, concentration-time data of CH_3SH and CH_3SCH_3 displayed no

Table 13. SUMMARY OF RESULTS OF DARK REACTIVITY EXPERIMENTS WITH NO_x

Compound	Date	$[\overline{HC}]$ (±1SD), ppmC	k_{HC}1/ hr^{-1}	$r^2$2/	$[NO_x]_{Initial}$ ppm	k_{NO_x}1/ hr^{-1}	$r^2$2/	$[NO]_{Initial}$ ppm	k_{expt}/k_{therm}2/	$r^2$4/
Furan	6-17-76	10.20 ± 0.15	—	—	1.182	43.8×10^{-3}	1.00	0.0	—	—
Thiophene	6-17-76	8.74 ± 0.05	2.73×10^{-3}	0.89	0.958	9.66×10^{-3}	—	0.0	—	—
Pyrrole	6-17-76	8.88 ± 0.46	21.5×10^{-3}	1.00	1.166	10.6×10^{-3}	0.81	0.004	—	—
CH_3SH	8-6-76	7.82 ± 0.41	—	—	1.095	10.3×10^{-3}	0.97	0.893	1.53	0.99
CH_3SCH_3	8-6-76	11.1 ± 0.04	—	—	1.159	9.21×10^{-3}	0.74	0.926	1.66	0.95
$(CH_3S)_2$	8-6-76	14.63 ± 0.83	20.9×10^{-3}	0.73	1.114	14.0×10^{-3}	0.71	0.875	1.87	0.95
COS	8-6-76	10.0 5/	—	—	1.106	8.26×10^{-3}	1.00	0.882	1.53	1.00
Control, NO_2	6-17-76	0.0	—	—	0.986	12.9×10^{-3}	1.00	0.0	—	—
NO	8-6-76	0.0	—	—	1.166	5.34×10^{-3}	—	0.943	1.22	—
NO	6-17-76	0.0	—	—	1.122	10.2×10^{-3}	0.99	1.062	1.56	1.00

1/ Rate constant for an assumed first order decay.

2/ Coefficient of determination for a least squares fit of ℓn C vs t.

3/ k_{expt} is the rate constant calculated from the data assuming a second order reaction; k_{therm} is the established rate constant for the thermal oxidation of NO at 300°K, $k_{therm} = 1.77 \times 10^{-2}\ ppm^{-1}\ hr^{-1}$ (ref.11).

4/ Coefficient of determination for k_{expt} as calculated from a least squares fit of $[NO]^{-1}$ vs t.

5/ Initial HC concentration is calculated based on injected volume.

apparent trends, and COS determinations were not performed. Methyl disulfide was observed to decay at a rate approximately twice that observed in the absence of NO_x. The NO_x decay rates for the control compared closely with those for CH_3SH, COS, CH_3SCH_3, and $(CH_3S)_2$. The ratios of NO oxidation rates, however, suggest that the presence of $(CH_2S)_2$ may enhance the NO oxidation rate slightly in comparison to the control values or those with CH_3SH, COS, or CH_3SCH_3.

These experiments indicate that CH_3SH, COS, CH_3SCH_3, and $(CH_3S)_2$ are all relatively unreactive with NO_x (mixtures of NO and NO_2). Among these species, methyl disulfide is probably the most reactive with NO_x, and its presence may enhance the NO oxidation rate slightly. In view of these results, the increased NO_x consumption noted earlier for irradiated mixtures of COS and NO_x are not due to thermal reactions with NO_x and may be attributed to light-induced reactions.

Overview of Bag Studies

A summary of half-lives of the six test compounds observed in each of the various test conditions is presented in Table 14. The half-lives for each test condition except the photooxidation experiments were calculated from first-order decay constants which were tabulated previously. The photooxidation half-lives are highly approximate and were calculated from data presented in Appendix B. These results may be used to reiterate previously stated observations. The stability of the heterocycles decreases from the "dark stability" to "dark phase reactivity with NO_x," to "light stability," to "dark phase reactivity with ozone," to the "photooxidation" experiments. The high reactivities of pyrrole with O_3 and furan with O_3 are clearly indicated. The stability of the alkyl sulfides in the presence of ozone is noteworthy, as is the enhanced decay rate of methyl disulfide on exposure to sunlight. The most significant observations, however, are dramatically illustrated by comparing the photooxidation half-lives with the other tabulated values. These results indicate that each of the test compounds can participate in atmospheric photooxidation reactions. Although many chemical reactions may contribute to the removal of these compounds from the atmosphere, these results suggest that photooxidation is a major pathway.

Table 14. SUMMARY OF TEST COMPOUND HALF-LIVES EXPRESSED IN HOURS

Experiment / Compound	Dark Stability[1]	Light Stability[2]	Dark Phase Reactivity with NO_x[3]	Dark Phase Reactivity with Ozone[4]	Photooxidation with NO_x[5]
Furan	420	65	—	2.9	0.20
Thiophene	880	42	250	23	3.5
Pyrrole	330	15	32	0.61	0.11
CH_3SH	—	—	—	140	1.8
CH_3SCH_3	72	57	—	70	1.1
$(CH_3S)_2$	78	3.2	33	270	0.33

[1] See Table 10.

[2] See Table 11.

[3] Calculated from k_{HC} values in Table 13.

[4] Assumes a constant O_3 concentration of 1 ppm; see Table 12.

[5] Calculated from HC behavior exhibited in the ozone-forming studies assuming a first order decay; see Appendix B for the tabulated, raw, concentration-time data.

CHAMBER STUDIES

Multiple-day experiments were conducted with furan, thiophene, pyrrole, methanethiol, methyl sulfide, methyl disulfide, and the control hydrocarbon, propylene, in the RTI Outdoor Smog Chamber Facility. A total of 20 smog chamber experiments was performed. The test compounds were chosen based on the results of ozone-formation screening tests conducted in Teflon bag reactors. Findings from the bag studies were presented and discussed in the previous subsection.

Target initial conditions for the smog chamber tests were 5.0 ppmC of the test compound and 1.0 ppm NO_x (20% NO_2). The initial HC/NO_x ratio of 5.0 was chosen to correspond to one of the two test conditions employed in the earlier bag screening tests and to correspond to the conditions required for maximum O_3 production from a highly reactive organic species such as propylene (ref. 27). These initial concentrations also correspond to those employed in outdoor smog chamber studies with a simulated urban mix conducted previously at RTI (ref. 9). Therefore, the chosen initial conditions allow convenient comparison with results from the urban mix runs.

The duration of each chamber experiment was 3 days. The object of a 3-day experiment is to simulate, roughly, the behavior of a photochemically reactive mixture of organics and NO_x which could occur in the atmosphere over several diurnal cycles.

Two types of smog chamber studies were conducted: static and dilution runs. In the static runs, the initial reactants were injected just prior to sunrise on the first day, and the photochemical reactions proceeded in the batch mode. Concentrations of reactant and product species were monitored for the 3-day run. The only dilution experienced by the reacting volume was due to sample replacement and chamber "breathing" caused by diurnal temperature variations and buffeting by winds.

The procedure employed for the dilution runs was similar to that used for the static runs except that the chamber contents were diluted with purified air at a fixed rate starting at 0800 EST on the first day. The dilution rate was chosen so that after 24 hours of operation, 95 percent of an unreactive tracer initially present would be removed. Dilution was terminated 24 hours after initiation, and the remaining 2 days of the run were conducted in the static mode. The object of dilution experiments was to simulate the dilution experienced by an air parcel in the atmosphere as it is transported downwind.

The data collected in the smog chamber studies are presented in the Appendixes. Concentration-time data are tabulated in Appendix D and are also presented in graphical form in Appendix E. Solar radiation profiles are also presented in Appendix E. Environmental parameters, initial conditions, and selected results from the 3-day chamber studies are summarized in Tables 15, 16, and 17. Day-one results are presented in Table 15, day-two results in Table 16, and day-three results in Table 17.

The variability of solar radiation and other environmental factors can make the results from outdoor smog chambers difficult to interpret. Three environmental parameters have been tabulated. Maximum daily temperature (T_{max}) and percent of possible minutes of direct sunshine (%SS) were measured at the Raleigh-Durham Airport. Daily irradiance (ΣSR) in Langleys (cal cm^{-2}) was calculated from total solar radiation data collected by EPA at a site 0.5 km from the chamber facility. These parameters are similar across most of the runs. The maximum temperatures ranged from 27 to 37° C (81 to 99° F). The %SS was generally greater than 60 percent, and the ΣSR was typically between 500 and 600 Langleys. This indicates that none of the run days was overcast and that most of the days experienced typical summertime irradiation for Piedmont North Carolina: sunny mornings with partly cloudy afternoons. This data provides only a broad assessment of the light conditions on each run day. The Appendixes D and E should be consulted for intensity-time data which can be used for comparison and interpretation of light history and corresponding specific chemical events.

The target initial conditions of 5.0 ppmC HC, 0.8 ppm NO, and 0.2 ppm NO_2 may be compared with the measured values listed in Table 15. The agreement is generally good, although three discrepancies should be noted. The thiophene injection on 8-17-76 in Chamber 2 is high by a factor of two; this was probably due to operator error. Comparison of target and measured initial concentrations for pyrrole and methanethiol reveals that in four out of five initial determinations, these compounds were not detected. This is somewhat surprising in view of the absence of such problems in the earlier bag studies. Concentration-time data for various reactants and products in the chamber runs, however, do confirm the presence of photochemically reactive species in the chambers after hydrocarbon injections. The observed difficulties may have arisen during injection, sampling, or analysis and remain to be resolved.

Table 15. SUMMARY OF SELECTED SMOG CHAMBER RESULTS--DAY 1

Hydrocarbon	Date	Dilution	Chamber	T_{max}, °C	ΣSS^a	ΣSR^b	$[HC]_i^c$	$[NO]_i^d$	$[NO_2]_i^d$	HC/NO_x	θ_{xo}^e	$[O_3]_{max}^{d,f}$	$t_{O_3}^g$	$[NO_x]_{1700}^{d,h}$	$x_{NO_x}^i$	$[SO_2]_{max}^{d,f}$	$t_{SO_2}^j$	$x_{SO_2}^k$
Furan	7/13-15/76	Static	1	32	93	661	4.72	0.797	0.217	4.7	2.85	0.746	9.13	0.043	0.958			
Thiophene			2				4.01	0.816	0.213	3.9	5.30	0.044	16.30	0.291	0.717	0.185	17.30	0.25[l]
Pyrrole			3				2.94	0.864	0.173	2.8	1.68	0.058	8.47	0.218	0.790	—	—	—
Propylene			4				5.16	0.688	0.175	6.0	2.90	1.125	15.63	0.192	0.778	—	—	—
Furan	8/17-19/76	Static	1	28	91	607	4.90	0.726	0.235	5.1	2.08	0.507	10.13	0.056	0.942	—	—	—
Thiophene			2				11.9	0.741	0.235	12.2	5.25	0.007	15.30	0.431	0.558	0.227	17.30	0.06[o]
Pyrrole			3				ND[m,n]	0.711	0.232	—	1.58	0.025	8.47	0.217	0.834	—	—	—
Propylene			4				5.23	0.648	0.215	6.1	1.90	0.969	15.63	0.223	0.742	—	—	—
Furan	7/20-22/76	95[p]	1	34	74	613	5.03	0.845	0.185	4.9	2.43	0.650	9.13	0.027	0.974	—	—	—
Thiophene			2				5.54	0.844	0.196	5.3	4.15	0.225	16.30	0.045	0.957	0.125	13.30	0.11
Pyrrole			3				ND[n]	0.770	0.186	—	1.70	0.058	8.47	0.043	0.955	—	—	—
Propylene			4				4.96	0.810	0.195	4.9	2.50	0.935	10.63	0.061	0.939	—	—	—
Methanethiol	7/28-30/76	Static	1	33	45	533	ND	0.798	0.210	—	2.67	0.745	10.13	0.071	0.930	1.610	10.13	0.32[o,q]
Methyl disulfide			2				ND	0.797	0.239	—	1.48	0.661	9.30	0.056	0.946	1.890	9.30	0.38[o,q]
Methyl sulfide			3				5.81	0.773	0.235	5.8	1.42	0.448	8.47	0.038	0.962	0.490	9.47	0.17[o]
Propylene			4				5.22	0.820	0.239	4.9	2.25	1.280	12.63	0.149	0.859	—	—	—
Methanethiol	8/10-13/76	95[p]	1	31	83	406	ND	0.752	0.246	—	2.60	0.713	10.13	0.022	0.978	1.021	10.13	0.20[o,q]
Methyl disulfide			2				7.17	0.768	0.249	7.1	1.20	0.629	9.30	0.027	0.973	1.230	8.30	0.17[o]
Methyl sulfide			3				5.24	0.783	0.247	5.1	1.15	0.468	8.47	0.013	0.987	0.357	8.47	0.14[o]
Propylene			4				4.14	0.782	0.199	4.2	2.17	0.951	10.63	0.095	0.903	—	—	—
Urban mix[r]	8/12-14/75	Static	3	32	71	545	3.81[s]	0.537	0.129	5.7	2.90	0.998	15.97	0.080	0.880	—	—	—
Urban mix[r]	7/28-30/75	95[p]	3	32	87	620	3.95[s]	0.545	0.170	5.5	2.88	0.668	14.97	0.037	0.948	—	—	—

[a] Percent possible minutes of direct sunshine measured at RDU airport (ref. 18).

[b] Summation of solar radiation for the day (daily irradiance), expressed in Langleys (cal cm^{-2}); measured by EPA, see text.

[c] Units = ppmC.

[d] Units = ppm.

[e] Time from first exposure to light (dawn in this case) until $NO-NO_2$ crossover, expressed in hours.

[f] Represents maximum observed concentration, not necessarily maximum attained concentration.

[g] Time of day of $[O_3]_{max}$, expressed in hours.

[h] Concentration of NO_x observed at 1700 EST.

[i] Fractional conversion (loss) of NO_x between dawn and 1700 EST.

[j] Time of day of $[SO_2]_{max}$, expressed in hours.

[k] x_{SO_2} is the yield of SO_2 determined at $[SO_2]_{max}$ and is a measure of molecules of SO_2 formed per molecule of consumed sulfur.

[l] Calculated based on a thiophene concentration estimated to be 1.0 ppmC at 17.3 hours.

[m] ND = not detected.

[n] Pyrrole peak could not be clearly resolved.

[o] Calculated based on an assumed zero concentration of the sulfur-containing compound at the time of $[SO_2]_{max}$.

[p] Dilution initiated at approximately 0800 EST on Day 1.

[q] Initial concentration assumed to be the target concentration of 5.0 ppmC.

[r] For original data see ref 9 .

[s] Determined as NMHC.

Table 16. SUMMARY OF SELECTED SMOG CHAMBER RESULTS--DAY 2

Hydrocarbon	Date	Dilution	Chamber	T_{max}, °C	%SS[a]	ΣSR[b]	$[O_3]_{min}$[c]	$[O_3]_{max}$[c]	t_{O_3}[d]	ΔO_3[c,e]	$[SO_2]_{min}$[c]	$[SO_2]_{max}$[c]	t_{SO_2}[f]	ΔSO_2[c,g]	%Day 1 ΔSO_2[h]
Furan	7/13-15/76	Static	1	32	83	576	0.173	0.194	15.13	0.021	--[i]	--	--	--	--
Thiophene			2				0.000	0.201	15.30	0.201	0.020	0.090	14.30	0.070	38
Pyrrole			3				0.000	0.043	15.47	0.043	--	--	--	--	--
Propylene			4				0.700	0.708	11.63	0.008	--	--	--	--	--
Furan	8/17-19/76	Static	1	29	93	601	0.122	0.208	15.13	0.086	--	--	--	--	--
Thiophene			2				0.000	0.132	16.30	0.132	0.017	0.191	16.30	0.174	77
Pyrrole			3				0.000	0.100	16.47	0.100	--	--	--	--	--
Propylene			4				0.609	0.698	14.63	0.089	--	--	--	--	--
Furan	7/20-22/76	95[j]	1	35	70	589	0.002	0.109	17.13	0.107	--	--	--	--	--
Thiophene			2				0.002	0.135	16.30	0.133	0.000	0.003	--	0.003	2
Pyrrole			3				0.000	0.101	16.47	0.101	--	--	--	--	--
Propylene			4				0.043	0.111	15.63	0.068	--	--	--	--	--
Methanethiol	7/28-30/76	Static	1	36	70	508	0.068	0.297	14.13	0.229	0.000	0.056	10.13	0.056	3
Methyl disulfide			2				0.084	0.313	14.30	0.229	0.000	0.000	--	0.000	0
Methyl sulfide			3				0.010	0.201	11.47	0.191	0.000	0.000	--	0.000	0
Propylene			4				0.430	0.538	13.63	0.108	--	--	--	--	--
Methanethiol	8/10-13/76	95[j]	1	32	88	584	0.004	0.168	16.13	0.164	0.000	0.027	14.13	0.027	3
Methyl disulfide			2				0.003	0.241	16.30	0.238	0.000	0.032	15.30	0.032	3
Methyl sulfide			3				0.002	0.169	16.47	0.167	0.000	0.014	12.47	0.014	4
Propylene			4				0.108	0.314	14.63	0.206	--	--	--	--	--
Urban mix[k]	8/12-14/75	Static	3	33	96	601	0.415	0.609	14.97	0.194	--	--	--	--	--
Urban mix[k]	7/28-30/75	95[j]	3	32	85	542	0.014	0.214	15.97	0.200	--	--	--	--	--

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[a] Percent possible minutes of direct sunshine measured at RDU airport (ref 18).

[b] Summation of solar radiation for the day (daily irradiance), expressed in Langleys (cal cm^{-2}); measured by EPA, see text.

[c] Units = PPM.

[d] Time of day of $[O_3]_{max}$, expressed in hours.

[e] Net ozone, $\Delta O_2 = [O_3]_{max} - [O_3]_{min}$.

[f] Time of day of $[SO_2]_{max}$, expressed in hours.

[g] Net sulfur dioxide, $\Delta SO_2 = [SO_2]_{max} - [SO_2]_{min}$.

[h] $(\Delta SO_2 \times 100)$/Day 1 $[SO_2]_{max}$.

[i] Nonapplicable entries are signified by blanks.

[j] Chambers operated in static mode after the termination of dilution at approximately 0800 EST on day 2.

[k] For original data see ref 9.

Table 17. SUMMARY OF SELECTED SMOG CHAMBER RESULTS--DAY 3

Hydrocarbon	Date	Dilution	Chamber	T_{max}, °C	%SS[a]	ΣSR[b]	$[O_3]_{min}$[c]	$[O_3]_{max}$[c]	t_{O_3}[d]	ΔO_3[c,e]	$[SO_2]_{min}$[c]	$[SO_2]_{max}$[c]	t_{SO_2}[f]	ΔSO_2[c,g]	%Day 1 ΔSO_2[h]
Furan	7/13-15/76	Static	1	37	76	544	0.085	0.162	14.13	0.077	--[i]	--	--	--	--
Thiophene			2				0.015	0.178	14.30	0.163	0.000	0.020	12.30	0.020	11
Pyrrole			3				0.002	0.196	13.47	0.194	--	--	--	--	--
Propylene			4				--	--	--	--	--	--	--	--	--
Furan	8/17-19/76	Static	1	27	92	586	0.065	0.172	14.13	0.107	--	--	--	--	--
Thiophene			2				0.000	0.173	14.30	0.173	0.005	0.035	13.30	0.030	13
Pyrrole			3				0.020	0.136	13.47	0.116	--	--	--	--	--
Propylene			4				0.377	0.400	13.63	0.023	--	--	--	--	--
Furan	7/20-22/76	95[j]	1	37	69	556	0.044	0.152	15.13	0.108	--	--	--	--	--
Thiophene			2				0.037	0.152	15.30	0.115	0.000	0.000	--	0.000	0
Pyrrole			3				0.033	0.147	15.47	0.114	--	--	--	--	--
Propylene			4				0.068	0.144	13.63	0.076	--	--	--	--	--
Methanethiol	7/28-30/76	Static	1	37	65	587	0.065	0.292	14.13	0.227	0.000	0.000	--	0.000	0
Methyl disulfide			2				0.085	0.324	15.30	0.239	0.000	0.000	--	0.000	0
Methyl sulfide			3				0.023	0.280	12.47	0.257	0.000	0.000	--	0.000	0
Propylene			4				0.226	0.317	14.63	0.091	--	--	--	--	--
Methanethiol	8/10-13/76	95[j]	1	33	66	607	0.043	0.200	15.13	0.157	0.000	0.012	15.13	0.012	1
Methyl disulfide			2				0.059	0.225	15.30	0.166	0.000	0.013	16.30	0.013	1
Methyl sulfide			3				0.068	0.183	14.47	0.115	0.000	0.007	16.47	0.007	2
Propylene			4				0.171	0.24[illegible]	14.63	0.075	--	--	--	--	--
Urban mix[k]	8/12-14/75	Static	3	33	79	569	0.246	0.474	14.97	0.228	--	--	--	--	--
Urban mix[k]	7/28-30/75	95[j]	3	31	59	437	0.038	0.190	13.97	0.152	--	--	--	--	--

[a] Percent possible minutes of direct sunshine measured at RDU airport (ref 18).

[b] Summation of solar radiation for the day (daily irradiance), expressed in Langleys (cal cm^{-2}); measured by EPA, see text.

[c] Units = ppm.

[d] Time of day of $[O_3]_{max}$, expressed in hours.

[e] Net ozone, $\Delta O_3 = [O_3]_{max} - [O_3]_{min}$.

[f] Time of day of $[SO_2]_{max}$, expressed in hours.

[g] Net sulfur dioxide, $\Delta SO_2 = [SO_2]_{max} - [SO_2]_{min}$.

[h] $(\Delta SO_2 \times 100)$/Day 1 $[SO_2]_{max}$.

[i] Nonapplicable entries are signified by blanks.

[j] Chambers operated in static mode after the termination of dilution at approximately 0800 EST on day 2.

[k] For original data see ref 9.

The injection temperature required for pyrrole (~131° C) was the highest of the three tested hydrocarbons. In addition, pyrrole is more sensitive to air oxidation than either thiophene or furan, and the pure liquid is known to oxidize readily in air (ref. 44). Rapid volatilization of liquid pyrrole in the heated injection manifold may have led to molecular decomposition. Furthermore, the use of stainless steel (tubing and pump) in the sampling system may have promoted sample modification or air oxidation of pyrrole. Finally, the GC column was not optimized for pyrrole, but was selected to allow analysis of many of the test species. Although a peak was observed on the GC trace at an appropriate retention time for pyrrole, it was not clearly resolved from surrounding peaks. The appreciable stability of pyrrole noted earlier in the bag studies suggests that the difficulties may have arisen either during the heated injection or during sampling.

Methanethiol was not detected during the runs which began on 7-28-76 and on 8-10-76. It is clear, however, that sulfur-containing species were injected on these dates, based on the measured maximum SO_2 concentrations presented in Table 15. On 7-28-76, neither methanethiol nor methyl disulfide could be clearly resolved from the GC records of initial analyses of Chambers 1 and 2. However, on 8-10-76, 7.17 ppmC of methyl disulfide was determined in Chamber 2, and a peak having a retention time similar to methyl disulfide was observed in Chamber 1. If the peak in Chamber 1 was from the disulfide, then the initially injected methanethiol was converted to and detected as approximately 3.8 ppmC of methyl disulfide. This apparent thiol-disulfide conversion may have occurred during either injection or sampling, although the possibility of conversion within the smog chamber cannot be completely ruled out. Methanethiol was injected as a pure gas at ambient temperature, and it may have been converted to the disulfide during injection.

Comparison of the chamber runs with the low HC/NO_x ratio bag studies presented earlier in Table 7 also supports the hypothesis of thiol to disulfide conversion. In the bag studies, methanethiol was clearly detected throughout the 1-day irradiation; the thiol system failed to achieve NO-NO_2 crossover and consequently produced very little ozone. The disulfide, however, was consumed quickly, achieved early NO-NO_2 crossover, and produced approximately 0.2 ppm of ozone in the bag studies. In contrast, the thiol and disulfide behaved similarly in the chamber studies: requiring short times to NO-NO_2 crossover and producing maximum day-one ozone concentrations of approximately 0.7 ppm.

Conclusive evidence defining the initial reactant identity or concentration conditions in the pyrrole and methanethiol smog chamber experiments is lacking. Results from these runs must be viewed with caution and must await additional chamber experiments with improved analytical capabilities before detailed interpretation can be undertaken.

First-Day Behavior

Many chemical transformations occur during the first day of each run. This is evidenced by the behavior of reactant and product concentration-time profiles presented in Appendix E. In addition, dilution is also initiated on the first day of each of the dilution runs. The following paragraphs will therefore address several characteristics of first-day behavior: NO-NO_2 crossover times, ozone formation, NO_x conversion, sulfur dioxide formation, and first-day dilution effects.

NO-NO_2 Crossover Times--

An indicator of the rate of the photochemical process is the time required from the first exposure to light (dawn in this case) until the concentrations of NO and NO_2 are equal. This parameter, θ_{xo}, is known as the NO-NO_2 crossover time and is tabulated for each run in Table 15.

Crossover times should not be influenced appreciably by dilution in runs involving highly reactive compounds which achieve rapid NO-NO_2 conversion. For these systems, crossover occurs near the time that dilution is initiated, and there is essentially no opportunity for dilution to influence the early chemical behavior which determines the time to reach crossover. This is supported by the results in Table 15. Except for thiophene, which was the slowest to reach crossover of the tested compounds, crossover times for the tested compounds are similar for both static and dilution runs.

The control hydrocarbon, propylene, required approximately 2.3 hours past dawn for crossover, while the less reactive urban mix required 2.9 hours. Furan behaved similarly to propylene in each of the three cases. Thiophene, as noted earlier, was the slowest of the tested compounds in promoting the photooxidation of NO and required over 5 hours to achieve $NO-NO_2$ crossover. Pyrrole was the fastest heterocycle and required only 1.7 hours to reach crossover. Among the alkyl sulfides, methanethiol was the least reactive. Methyl sulfide and methyl disulfide behaved similarly and exhibited the shortest crossover times of the tested compounds.

Ozone Formation--

The maximum first-day ozone concentration, $[O_3]_{max}$, and the time of day that it was observed are tabulated for each chamber run in Table 15. In addition to the chamber experiments, replicate bag studies were conducted concurrently with the chamber runs on two occasions. Data from the bag experiments are compiled in Appendix B, and $[O_3]_{max}$ data are compared for selected bag and day-one static chamber runs in Table 18. These results show reasonable agreement in all cases except for pyrrole and methanethiol. Similar discrepancies for these two compounds, as noted in earlier discussions, were tentatively attributed to injection anomalies in the chamber runs.

The results in Table 15 indicate that in the chamber runs propylene produced the highest level of ozone, approximately 1.0 ppm. The static urban mix run also produced approximately the same amount. Furan produced the highest level of ozone among the heterocycles with maximum values ranging from 0.51 to 0.75 ppm. The static thiophene run produced less ozone than any of the other tested compounds and did not exceed the NAAQS of 0.08 ppm. Although the results for pyrrole and methanethiol may be questionable, low levels of ozone were produced in the chamber into which pyrrole had been injected, and maximum ozone levels of 0.70 to 0.75 ppm were found in the methanethiol runs. Methyl disulfide produced approximately 0.65 ppm ozone and methyl sulfide produced slightly less, 0.45 ppm.

Maximum ozone concentrations were achieved in the afternoon between 1300 and 1600 EST for static propylene runs. The urban mix behaved similarly and achieved $[O_3]_{max}$ at 1600. The ordering of the times to $[O_3]_{max}$ for the remaining test compounds roughly duplicated that for the times to $NO-NO_2$ crossover. Thiophene, the slowest compound to crossover, achieved $[O_3]_{max}$ after 1500; the other five compounds reached $[O_3]_{max}$ by 1000.

NO_x Conversion--

Based on NO_x concentrations determined prior to dawn at the start of a run and at 1700 EST, fractional NO_x conversions, X_{NO_x}, were calculated

Table 18. COMPARISON OF OZONE FORMATION IN BAG AND CHAMBER STUDIES

Compound	Chamber $[O_3]_{max}$	Bag $[O_3]_{max}$
Furan[1/]	0.507	0.952
Thiophene[1/]	0.007	0.0
Pyrrole[1/]	0.025	0.290
Propylene[1/]	0.969	1.113
CH_3SH[2/]	0.745	0.015
$(CH_3S)_2$[2/]	0.661	0.594
CH_3SCH_3[2/]	0.448	0.580
Propylene[2/]	1.280	0.945

[1/] Experiments Conducted on 8-17-76.

[2/] Experiments conducted on 7-28-76.

for day-one results. Conversion is the fraction of the initial NO_x that cannot be accounted for as either NO or NO_2 at 1700 EST. It should be noted that the chemiluminescent NO_x readings were not corrected for interferences, and therefore the values represent not only NO and NO_2, but also other nitroxy species such as PAN, which may be detected as NO_2 (ref. 21).

Conversions of 75 to 85 percent were observed for static propylene runs, and slightly higher values were observed in the urban mix runs. Thiophene, because of its reduced reactivity in comparison to the other test compounds, consumed only 60 to 70 percent of the initial NO_x. In contrast, furan, methanethiol, methyl disulfide, and methyl sulfide consumed approximately 95 percent of the initial NO_x by 1700. Based on the NO_2 concentration-time profiles shown in Appendix E, the alkyl sulfides consume NO_x more quickly than does furan. For the sulfides, within an hour after $[O_3]_{max}$ (~1100 EST), the $[NO_2]$ has dropped to low levels, and approximately 90 percent of the NO_x has been consumed.

Free radical reactions resulting in the formation of PAN and nitric acid are considered to be the major chemical sinks for NO_x in classical hydrocarbon-NO_x photochemical systems (ref. 4) and may be responsible for the loss of NO_x in the propylene, urban mix, and furan experiments. It is more difficult to speculate on the mechanism for NO_x removal during the pyrrole and thiophene runs. For the alkyl sulfides, the mechanism for NO_x removal is also unclear, although it may be postulated to involve reactive free radicals which are generated by photooxidation processes. The identity of these radicals is unknown at this time. In view of the molecular structure of the sulfides, however, PAN formation seems unlikely. Future studies will be required to determine if the observed NO_x conversion is due to scavenging by organosulfoxy radicals, incorporation into particles, or some as yet undefined mechanism.

Sulfur Dioxide Formation--

Each of the sulfur-containing species tested in the chambers produced SO_2 as a product of photooxidation as indicated by pulsed UV fluorescence detection. Maximum observed SO_2 concentration, $[SO_2]_{max}$; the corresponding time that the maximum was observed, t_{SO_2}; and the SO_2 yield, X_{SO_2}, (molecules of SO_2 formed per molecule of consumed sulfur at the time of the $[SO_2]_{max}$) are presented in Table 15 for both static and dilution runs. In addition, concentration-time profiles depicting NO, NO_2, O_3, and SO_2 first-day behavior for thiophene, methyl disulfide, and methyl sulfide-static runs are presented in Figures 9, 10, and 11. Figure 12 presents NO, NO_2, and O_3 data from a propylene run for comparison. The methanethiol run, due to previously noted questions, is not considered in this comparison. However, concentration profiles for methanethiol, found in Appendix E, display the same general features as are depicted by the disulfide profiles.

Thiophene produced the smallest quantities of SO_2 of the sulfur-containing compounds tested in the chambers. On 7-13-76 the $[SO_2]_{max}$ for thiophene corresponds to an approximate yield of 0.25. The increased $[SO_2]_{max}$ on 8-17-76 in comparison to the value on 7-13-76 is due to the three-fold increase in the initial thiophene concentration. In addition to the increased $[SO_2]_{max}$ on 8-17-76, a reduced SO_2 yield, 0.08, was observed. The thiophene determinations shown in Appendix C indicate that a significantly larger fraction of thiophene was consumed on the first day in the 8-17-76 run than in the 7-13-76 run. In contrast, increased SO_2 production was noted on the second and third days of the 8-17-76 run. These observations suggest that the photooxidation of thiophene may produce a rather long-lived sulfur-containing intermediate which can be further oxidized to SO_2 on the second and third days.

Substantial amounts of SO_2 were produced by the alkyl sulfides on 7-28-76. Methyl disulfide and methanethiol produced 1.9 and 1.6 ppm of SO_2 corresponding to approximate yields of 0.4 and 0.3. Although methyl sulfide produced somewhat lower values, an $[SO_2]_{max}$ of 0.5 ppm and a yield of 0.2, this may be due to differences in the initial conditions. The initial concentration of sulfur in this experiment was approximately one half of the level employed in the thiol and disulfide runs.

The general shape of the SO_2 profiles may be examined in Figures 9, 10, and 11. Sulfur dioxide was detected as a reaction product simultaneously with the onset of NO oxidation. As the NO oxidation rate increases, so does the production rate of SO_2. The largest increase in SO_2 concentration appears to occur between the time of NO-NO_2 crossover and the time of the ozone maximum. The concentration profiles indicate that $[SO_2]_{max}$ and $[O_3]_{max}$ are achieved at approximately the same time. The $[SO_2]_{max}$ for the slow-reacting thiophene occurs late in the day, at 1700 EST. Peak SO_2 concentrations for the fast-reacting alkyl sulfides occur around 1000 EST. These observations suggest that the same radicals which are responsible for NO oxidation and ozone formation by these sulfur-containing compounds are by analogy also responsible for the concurrent SO_2 formation.

After the maxima, SO_2 and O_3 profiles are approximately parallel for the next few hours. Near dusk, however, a marked difference in O_3 and SO_2 behavior occurs. Whereas the O_3 continues to decay at approximately the same rate into the night as it did in the afternoon, the SO_2 decay rate increases sharply. An inflection point occurs shortly after sundown at approximately 2000 EST. There are several possible explanations for this phenomenon.

1. If SO_2 continues to be produced photochemically after $[SO_2]_{max}$, then the slow decay until sundown represents only a small imbalance between the relative strengths of the source and sink mechanisms. After sundown, the photochemical source strength is reduced to zero, and the sink dominates the behavior.
2. A similar explanation can be postulated to involve a light-mediated equilibrium between SO_2 and other as yet undefined species.

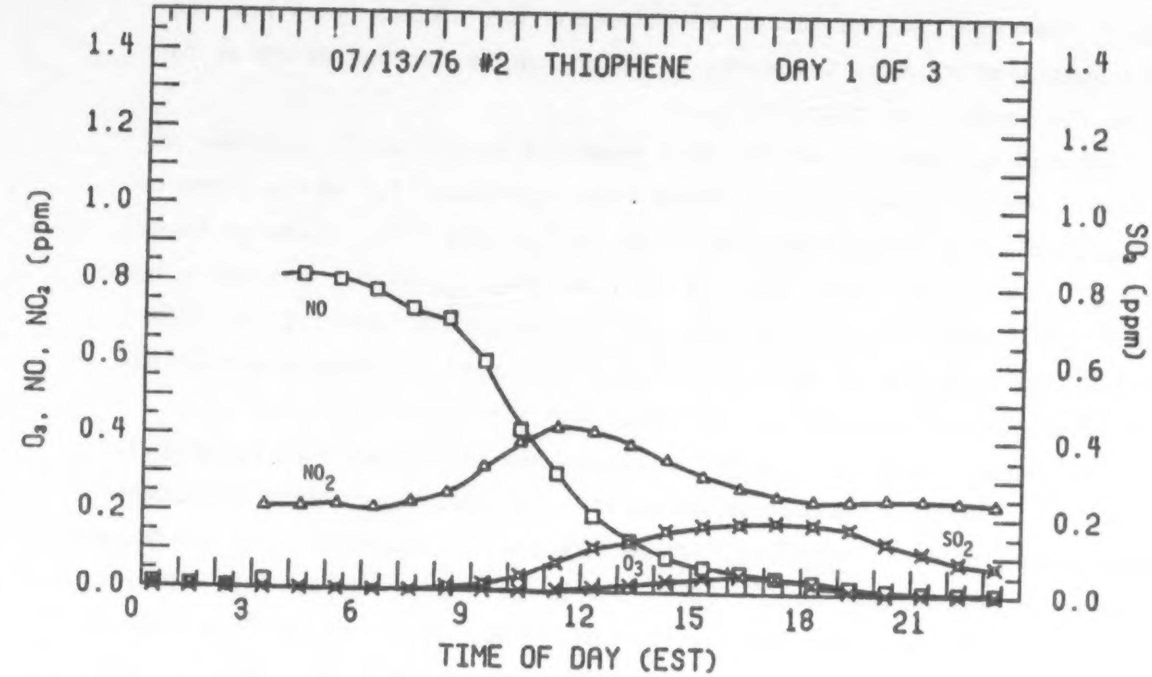

Figure 9. Concentration profiles for first day (7-13-76) of thiophene-NO_x static smog chamber experiment. Initial conditions: 4.01 ppmC thiophene; 0.816 ppm NO; 0.213 ppm NO_2 in RTI outdoor smog chamber No. 2.

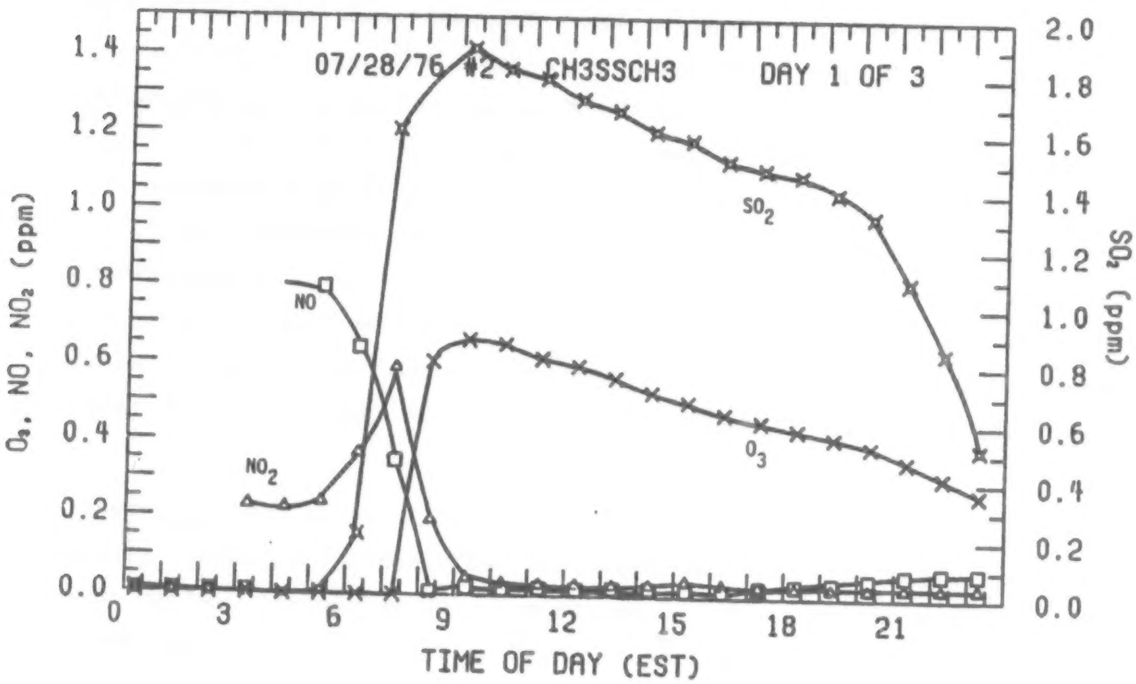

Figure 10. Concentration profiles for first day (7-28-76) of methyl disulfide-NO_x static smog chamber experiment. Initial conditions: 5.0 ppmC (target) methyl disulfide; 0.797 ppm NO; 0.239 ppm NO_2 in RTI outdoor smog chamber No. 2.

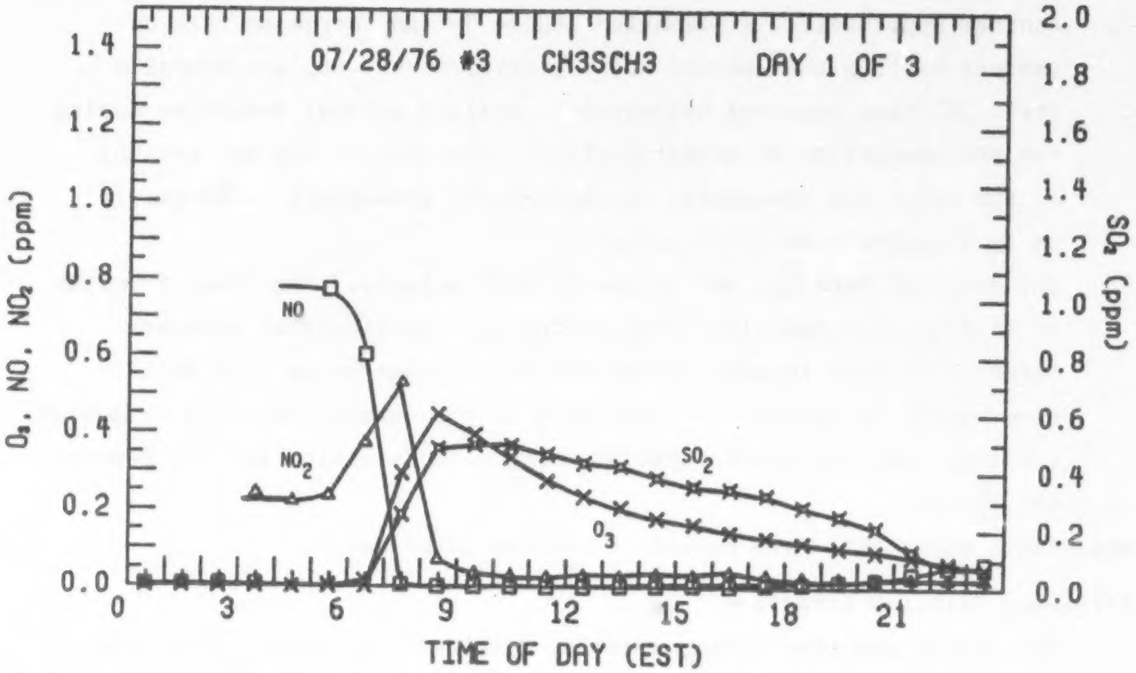

Figure 11. Concentration profiles for first day (7-28-76) of methyl sulfide-NO$_x$ static smog chamber experiment. Initial conditions: 5.81 ppmC methyl sulfide; 0.773 ppm NO; 0.235 ppm NO$_2$ in RTI outdoor smog chamber No. 3.

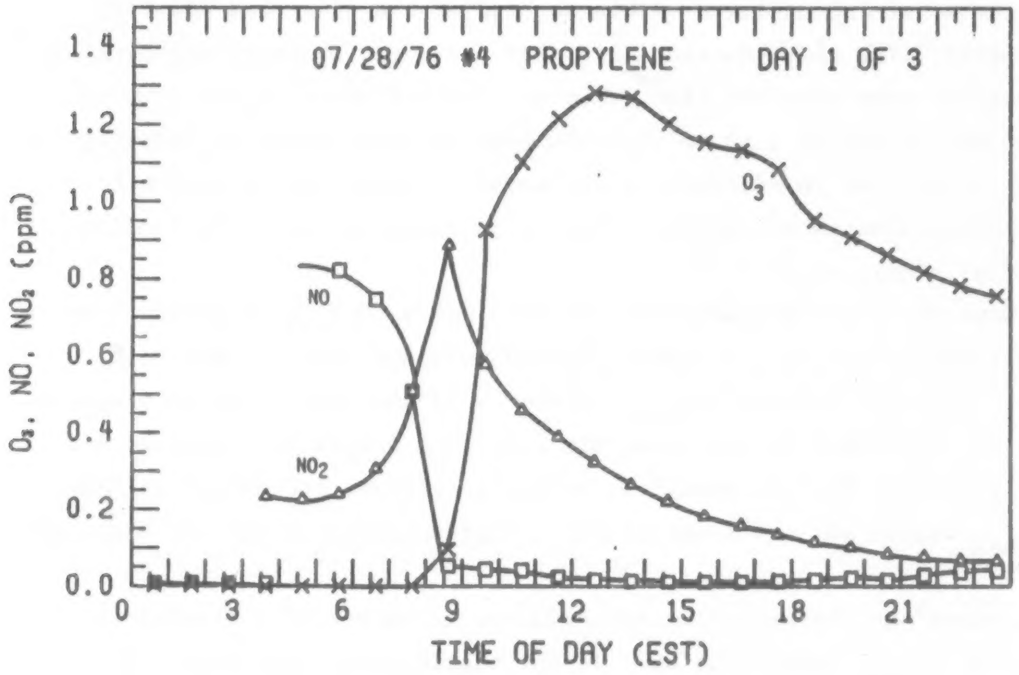

Figure 12. Concentration profiles for first day (7-28-76) of propylene-NO$_x$ static smog chamber experiment. Initial conditions: 5.22 ppmC propylene; 0.820 ppm NO; 0.239 ppm NO$_2$ in RTI outdoor smog chamber No. 4.

3. Another hypothetical explanation relies on the increased rate of ambient cooling that occurs shortly after dark. Cox and Sandalls (ref. 34) have observed hygroscopic, sulfate aerosol formation during the photooxidation of methyl sulfide. The natural ambient cooling of the humid and presumably particle-laden atmosphere could result in an enhanced rate of SO_2 loss.
4. The observed behavior may be due to wall effects. The chamber volume is stirred continuously. This mixing may facilitate an exchange between the bulk chamber volume and the chamber walls. If wall temperature is reduced in comparison to the chamber contents by ambient cooling, then increased rates of surface condensation and SO_2 removal may result.

Additional experiments are needed to resolve these points.

First-Day Dilution Effects--

The highly reactive furan, pyrrole, methanethiol, methyl disulfide, methyl sulfide, propylene, and urban mix, achieved NO-NO_2 crossover within 3 hours after dawn and exhibited similar crossover times for both dilution and static runs. This is not surprising, because, for these compounds, crossover was achieved within an hour of the time that dilution was initiated. The slow-reacting thiophene, however, achieved crossover 1 hour earlier with dilution than without. The reduction of the time to crossover may be due in part to the role that dilution plays in reducing the NO concentration in addition to the normally occurring reduction of [NO] by photooxidation processes. This is in agreement with the findings of Fox et al. (ref. 45).

In general, the compounds that achieved early $[O_3]_{max}$ in static runs produced similar, but only slightly reduced, maximum ozone levels with dilution. Dilution reduced $[O_3]_{max}$ levels by 17 and 26 percent in propylene runs and by 33 percent in the urban mix runs. No trends are apparent with furan or pyrrole. For methanethiol, methyl disulfide, and methyl sulfide the $[O_3]_{max}$ values were constant within ± 5 percent for static and dilution runs.

Thiophene was the exception and produced in excess of a fivefold increase in $[O_3]_{max}$ with dilution. In the static runs, less than 0.05 ppm O_3 was formed; whereas, the first-day $[O_3]_{max}$ was increased significantly to 0.23 ppm for the dilution run. It is recognized that the behavior of maximum levels of ozone is highly nonlinear with respect to precursor concentrations. Nonlinear behavior with dilution has also been noted in this laboratory: dilution of an O_3-producing photochemical system does not reduce the $[O_3]_{max}$ in direct proportion to the extent of dilution (ref. 9). The characteristics of the thiophene run are similar to another documented observation of an increased $[O_3]_{max}$ with dilution (ref. 45). Obtaining this behavior apparently requires a slow-reacting test compound or initial conditions which promote slow behavior.

The time required to achieve $[O_3]_{max}$ for propylene was reduced with dilution. Ozone maxima occurred after 1300 EST in the static runs and occurred prior to 1100 with dilution. For the other compounds, the times to $[O_3]_{max}$ were not sensitive to dilution. It is likely that the compounds that achieved early $[O_3]_{max}$ values were unaffected by dilution because the maxima were achieved near the time that dilution was initiated. The $[O_3]_{max}$ for thiophene under both static and dilution conditions occurred late in the solar day. The decrease in light intensity in the afternoon was probably a major factor in determining the time of $[O_3]_{max}$ in both of these runs.

Maximum SO_2 concentrations and yields were reduced by approximately 33 percent under dilution conditions. For the fast-reacting alkyl sulfides, the time to achieve $[SO_2]_{max}$ was relatively insensitive to dilution and was reduced by approximately 1 hour with dilution. In the thiophene runs, although timing of the $[O_3]_{max}$ was insensitive to dilution, the time of $[SO_2]_{max}$ was reduced by 4 hours with dilution. Ozone is formed by a chain reaction formation mechanism, which can continue to generate O_3 in spite of simultaneous precursor removal. Although SO_2 formation may also involve reactions of chain-generated free radicals, SO_2 production is limited by the amount of sulfur initially present in the reacting mixture. Dilution should, therefore, exert a pronounced effect on the timing of $[SO_2]_{max}$ for the slow-reacting thiophene.

Second- and Third-Day Effects

Selected second- and third-day results for the chamber runs are presented in Tables 16 and 17. A key parameter in these results is the net ozone, ΔO_3, produced during each day. Net ozone is calculated for any one day by subtracting the morning minimum ozone concentration from the maximum ozone concentration achieved on that day ($\Delta O_3 = [O_3]_{max} - [O_3]_{min}$). The net ozone and the maximum values are identical on the first day because the morning minimum is zero. Net ozone concentrations are summarized in Table 19 for each day of both static and dilution experiments.

Ozone Formation--

In the static experiments, propylene generated the largest first-day ΔO_3 levels of the tested compounds. Ozone concentration on the second and third days of the propylene experiments, however, tended to decay from the elevated first-day levels, and synthesis was indicated by only small values of ΔO_3. Furan behaved similarly to propylene and generally produced second- and third-day ΔO_3 values of less than 0.10 ppm. On the third day, furan produced ΔO_3 values that tended to be slightly larger than second-day values.

Although the pyrrole results may be questionable, as was noted earlier, trends in the ΔO_3 values are evident. In both the static and dilution runs, net ozone levels increased from the first, to the second, to the third day. The NO concentration in the pyrrole experiments displayed a marked increase after the NO_2 peak on 7-13-76 and 8-17-76 (see the concentration profiles in Appendix E). Although the trends observed in net ozone cannot be explained, they may be related to the peculiar NO behavior noted above.

The open-chain sulfur species produced not only ΔO_3 values of 0.4 to 0.7 ppm on the first day, but also considerable amounts of ozone on the subsequent days. Methanethiol and methyl disulfide produced approximately equal quantities on the second and third days, 0.23 ppm. The net ozone produced on the third day exceeded the second-day value by only 0.01 ppm in the methyl disulfide runs; whereas, a more substantial excess of 0.07 ppm was noted for methyl sulfide.

In contrast to the other test compounds, thiophene produced more ozone in static runs on the second day than on the first day. In two separate static experiments thiophene produced net ozone levels of 0.20 and 0.13 ppm on the second days in comparison to the first day values of 0.04 and 0.01. This is over a fivefold increase from the first to the second days. Figure 13 depicts O_3 profiles for thiophene runs conducted under static and dilution conditions. The second-day increase in ozone is dramatically illustrated

Table 19. NET OZONE PRODUCED IN BOTH STATIC AND DILUTION CHAMBER RUNS

Compound	Operation[2]	Net Ozone (ΔO_3),[1] ppm		
		Day 1	Day 2	Day 3
Furan	S[3,4] D[5]	0.746, 0.507 0.650	0.021, 0.086 0.107	0.077, 0.107 0.108
Thiophene	S[3,4] D[5]	0.044, 0.007 0.225	0.201, 0.132 0.133	0.163, 0.173 0.115
Pyrrole	S[3,4] D[5]	0.058, 0.025 0.058	0.043, 0.100 0.101	0.194, 0.116 0.114
Methanethiol	S[6] D[7]	0.745 0.713	0.229 0.164	0.227 0.157
Methyl Disulfide	S[6] D[7]	0.661 0.629	0.229 0.238	0.239 0.166
Methyl Sulfide	S[6] D[7]	0.448 0.468	0.191 0.167	0.257 0.115
Propylene	S[3,4,6] D[5,7]	1.125, 0.969, 1.280 0.935, , 0.951	0.008, 0.089, 0.108 0.068, , 0.206	—[10], 0.023, 0.091 0.076, , 0.075
Urban Mix	S[8] D[9]	0.998 0.668	0.194 0.200	0.228 0.152

[1] Results are summarized from Tables 15, 16, and 17.

[2] S = Static run; D = Dilution run.

[3] First entry under each day from experiment conducted on 7/13-15/76.

[4] Second entry under each day from experiment conducted on 8/17-19/76.

[5] First entry under each day from experiment conducted on 7/20-22/76.

[6] Entry from experiment conducted on 7/28-30/76.

[7] Entry from experiment conducted on 8/10-13/76.

[8] Entry from experiment conducted on 8/12-14/75.

[9] Entry from experiment conducted on 7/28-30/75.

[10] Ozone decayed monotonically and therefore a ΔO_3 could not be determined.

for the static run. Third-day ozone levels are reduced only slightly from the second-day levels. It may be postulated that the increased second- and third-day ozone levels were due to the low reactivity of thiophene. Because most of the first-day sunlight was required for photooxidation of NO, the low first-day ozone levels were probably limited by the duration of irradiation. On the second day, [NO_2] exceeded [NO], and the remaining thiophene, along with any remaining reactive intermediates generated on the first day, apparently existed in quantities conducive for substantial ozone generation.

One of the causes of the high rural oxidant problem may be the transport of a partially spent system of ozone precursors from urban areas. In such systems, low reactivity hydrocarbons and reactive intermediates are likely to play a significant role in ozone generation within an air parcel on the second and third days downwind from the source. A possible example is seen in the ΔO_3 values from the urban mix experiments presented in Table 19. The sulfur-containing compounds exhibit ΔO_3 behavior similar to the urban mix, suggesting that such compounds can also exert a significant influence on ozone formation downwind from sources.

A comparison of the times required to achieve $[O_3]_{max}$ on each day can be made from the results of Tables 15, 16, and 17. The time to reach $[O_3]_{max}$ was delayed by up to 6 hours on the second day relative to the first day. Thiophene, however, exhibited no appreciable differences in the times to $[O_3]_{max}$. In most cases, day-two and day-three $[O_3]_{max}$ occurred after 1400 EST. For the heterocycles in static runs, second-day $[O_3]_{max}$ occurred later in the afternoon than the third-day $[O_3]_{max}$ values. The open chain sulfides, however, exhibited no appreciable timing differences between days two and three. Dilution had a noticeable effect on the day-two times of $[O_3]_{max}$, delaying their occurrence by an hour in comparison to those on the third day. In comparison with the static runs, dilution delayed the time of $[O_3]_{max}$ on both the second and third days. Explanations for these observations are not immediately apparent.

The effects of dilution on net ozone production may be examined using the results in Table 19. In general, the net ozone levels generated on the first day exceed those produced on the second and third days. In most cases, second-day levels are slightly higher than third-day levels. This may suggest a decrease in ozone production on subsequent days downwind from sources of these compounds. Although most ΔO_3 levels in dilution runs are reduced in comparison to static values, they are never reduced in proportion to the extent of dilution and are generally reduced by less than 40 percent. This finding demonstrates the nonlinear behavior of ozone formation in air parcels which are experiencing dilution.

Fuel conversion technology is in the early stages of its development. Additional research is required to define future emissions rates of the tested compounds from fuels-conversion facilities. The degree to which our experiments will mimic areas downwind from such facilities is therefore also uncertain. Nevertheless, the test compounds, with the exception of propylene, produced net ozone levels in excess of the NAAQS of 0.08 ppm on the second and third days in both static and dilution experiments. This suggests that under the proper conditions, the tested compounds can have a considerable impact on ozone levels generated downwind from the point of their emission. The behavior of these compounds should therefore be considered in detail if significant anthropogenic sources are to be constructed.

Sulfur Dioxide Formation--

Each of the sulfur-containing compounds produced considerable quantities of SO_2 as a reaction product. Among these compounds, only thiophene produced significant quantities of SO_2 on the second and third days. Maximum SO_2 levels achieved on days two and three are presented in Tables 16 and 17.

The open-chain sulfides apparently react quickly, exhausting the initially present sulfur compound by the end of the first day. In the static runs, maximum SO_2 levels between 0 and 60 ppb were generally observed on the second day. Peak concentrations on the third day ranged from 0 to 15 ppb. The net SO_2, ΔSO_2, produced on the second and third days are generally less than 3 percent of the day-one values.

Thiophene, as noted previously, reacts more slowly than the tested open-chain sulfides. Figure 14 presents SO_2 profiles for thiophene runs conducted under static and dilution conditions. In the 7/13-15/76 static experiment, ΔSO_2 values on the second and third day correspond to 38 percent and 11 percent of the first day maximum. These percentages are significantly larger than the 3 percent noted earlier for the alkyl sulfides and emphasize the increased multiple-day SO_2 production potential of thiophene.

The above observations indicate that the slow-reacting sulfur compound, thiophene, can produce significant quantities of both O_3 and SO_2 in multiple-day static irradiations. Although particle formation was not investigated in this study, it is likely that sulfate aerosol is formed in the photo-oxidation of the sulfur-containing compounds. Emission levels of thiophene are poorly defined, although they are expected to be low. The results of this study suggest that if emissions from future fuel conversion facilities include sulfur-containing organics such as thiophene, then under stagnant conditions, local areas face the possibility of reduced air quality in the form of increased levels of O_3, SO_2, and sulfate aerosols.

Dilution reduced the maximum SO_2 concentrations achieved by the sulfur-containing species on the first day by 33 percent in comparison with the static runs. Net SO_2 levels on subsequent days were reduced to essentially zero by dilution. The extreme sensitivity of $[SO_2]$ behavior to dilution is clearly evident in Figure 14 and may be contrasted to the ozone profiles shown in Figure 13 for the same runs. As noted earlier, the different

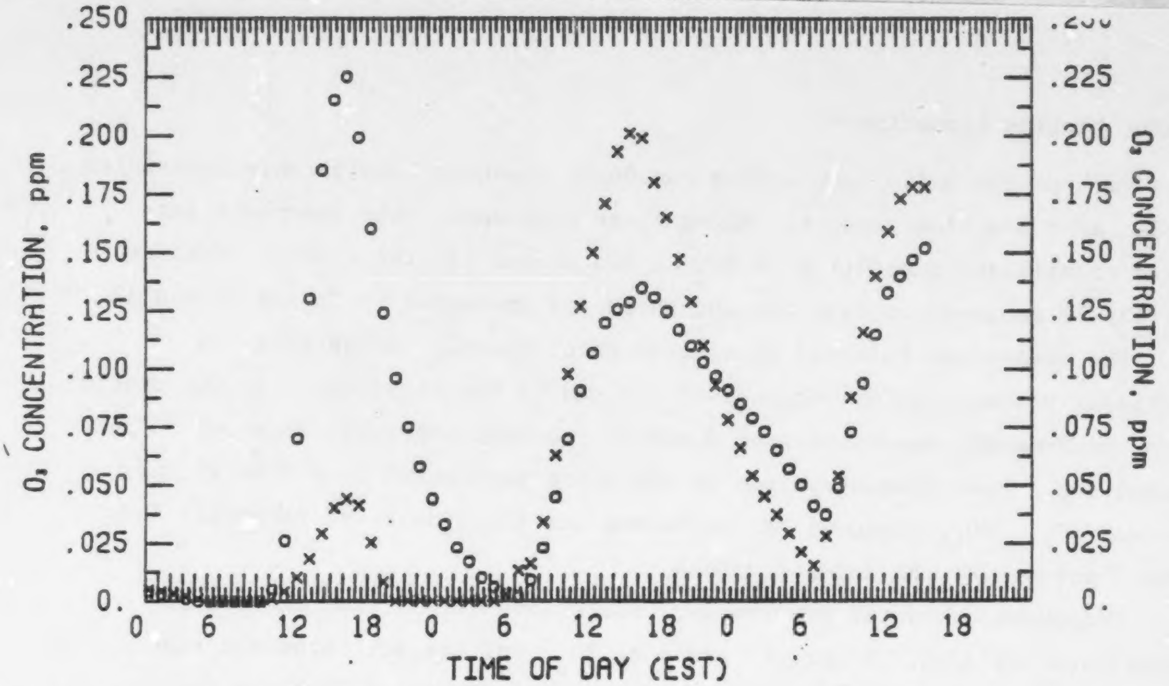

Figure 13. Ozone concentration profiles for three-day thiophene-NO_x runs conducted in RTI outdoor smog chamber No. 2. Static run (×) 7/13-15/76; initial conditions: 4.01 ppmC thiophene and 1.029 ppm NO_x. Dilution run (○) 7/20-22/76; initial conditions: 5.54 ppmC thiophene and 1.040 ppm NO_x; dilution was started at 0800 EST, 7/20 at a rate such that 95% of the original chamber contents would be replaced by purified air when dilution was stopped at 0800 EST, 7/21.

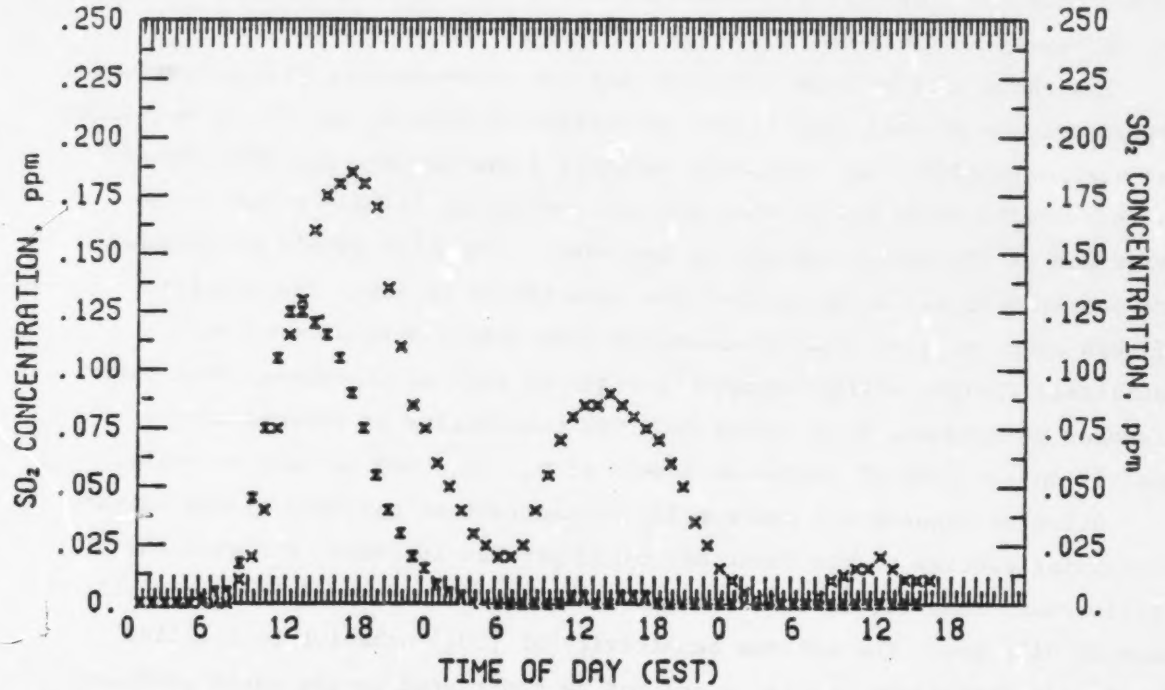

Figure 14. Sulfur dioxide concentration profiles for three-day thiophene-NO_x runs conducted in RTI outdoor smog chamber No. 2. Static run (x) 7/13-15/76; initial conditions: 4.01 ppmC thiophene and 1.029 ppm NO_x. Dilution run (x) 7/20-22/76; initial conditions: 5.54 ppmC thiophene and 1.040 ppm NO_x; dilution was started at 0800 EST, 7/20 at a rate such that 95% of the original chamber contents would be replaced by purified air when dilution was stopped at 0800 EST, 7/21.

shapes of these curves suggest different mechanisms of SO_2 and O_3 formation. Although SO_2 may be formed by oxidation steps involving reactions with free radicals which are generated by photochemical chain reactions, the maximum SO_2 levels are limited by the initial amount of the sulfur-containing reactant. In contrast, photochemical chain reactions can produce many molecules of ozone for each consumed precursor molecule. The efficiency of this process changes not only with absolute concentration of the ozone precursors, hydrocarbons, and NO_x, but with their ratio as well. The results of Figures 13 and 14 are perhaps the first to contrast the reactant-limited behavior of a secondary pollutant, in this case SO_2, with the simultaneous nonlinear precursor-product behavior of the secondary pollutant, ozone.

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APPENDIX A

Environmental Conditions
for Irradiated Bag
and Chamber Studies

APPENDIX A. ENVIRONMENTAL CONDITIONS FOR IRRADIATED BAG AND CHAMBER STUDIES

Date	Type of Study[a]	Time of Initial Exposure, EST	T_{max} °C	%SS[b]	ΣSR_{12}[c]	ΣSR[d]
6-2-76	B	0900	29	32	150	376
6-8-76	B	0945	32	89	165	646
6-9-76	B	1000	33	40	144	491
6-10-76	B	0820	33	28	226	470
6-22-76	B	0925	29	24	116	404
6-29-76	B	1002	33	66	152	633
7-1-76	B	0945	29	55	170	516
7-13-76	C	0505[e]	32	93	—[f]	661
7-14-76	C	0505[e]	32	83	—	576
7-15-76	C	0505[e]	37	76	—	544
7-16-76	B	1035	35	71	110	581
7-20-76	C	0515[e]	34	74	—	613
7-21-76	C	0515[e]	35	70	—	589
7-22-76	C	0515[e]	37	69	—	556
7-23-76	B	0920	34	34	152	481
7-28-76	C,B	0525[e]	33	45	241	533
7-29-76	C	0525[e]	36	70	—	508
7-30-76	C	0525[e]	37	65	—	587
8-10-76	C	0535[e]	31	83	—	406
8-11-76	C,B	0535[e]	32	88	268	584
8-12-76	C	0535[e]	33	66	—	607
8-17-76	C,B	0540[e]	28	91	265	607
8-18-76	C	0540[e]	29	93	—	601
8-19-76	C,B	0540[e]	27	92	283	586

[a] B = Bag Study; C = Chamber Study

[b] Percent possible minutes of direct sunshine measured at RDU Airport.

[c] Summation of solar radiation from beginning the bag exposure until 1200 EST; expressed in Langleys (cal cm^{-2}); measured at EPA.

[d] Summation of solar radiation for the day (daily irradiance); expressed in langleys (cal cm^{-2}); measured at EPA.

[e] Dawn; based on solar radiation data; accurate to ±10 minutes.

[f] Nonapplicable entries are denoted by blanks, "__".

APPENDIX B

Results of Bag Studies

Appendix B. RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppm C	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
5-25 to 5-28-76	1415 (5-25)	10.8						
Dark stability	1700	10.7						
Furan	0950 (5-26)	10.8						
1300 (5-25), injection	0930 (5-27)	10.0						
	1100	10.4						
	1115	10.6						
	0930 (5-28)	9.60						
	1315	9.58						
5-26 to 6-1-76	1300 (5-26)	9.80						
Dark stability	1000 (5-27)	9.67						
Thiophene	1130	10.1						
1145 (5-26), injection	1300	9.88						
	1000 (5-28)	9.88						
	1330	9.53						
	1330 (6-1)	8.88						
5-27 to 6-1-76	1600 (5-27)	11.2						
Dark stability	0900 (5-28)	10.3						
Pyrrole	1300	9.92						
1500 (5-27), injection	1000 (6-1)	8.58						
6-2-76	0745	9.62	0837	1.37	0.310	1.680		
Ozone formation	1120	—	1054	—	0.572	0.572	1.067	
Furan	1340	—	1232	—	0.456	0.456	1.133	
0900		—	1410	—	0.280	0.280	1.075	
6-2-76	0815	10.4	0844	0.370	0.075	0.445		
Ozone formation	1140	1.38	1110	—	0.148	0.148	0.107	
Furan	1345	0.61	1245	—	0.130	0.130	0.092	
0900	1455	0.48	1415	—	0.114	0.114	0.096	
6-2-76	0820	9.0	1046	—	—	—	—	
Light stability	1100	8.62	1220	—	—	—	—	
Furan	1325	8.53	1402	—	—	—	—	
0900	1440	8.38						
6-2-76			0833	1.380	0.300	1.680		
NO oxidation (light)[c]			1100	1.280	0.372	1.652	—	
NO, NO_2			1255	1.246	0.372	1.618	—	
0900 (light)			1442	1.200	0.390	1.590	—	
6-2 to 6-3-76	1255 (6-2)	2.27	1050 (6-2)				0.813	
Dark reactivity with O_3	1520	1.36	1237				0.769	
Furan	0950 (6-3)	0.37	1330				0.639	
1225 (6-2), furan injection	1125	0.32	1500				0.524	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
6-2 to 6-3-76	1320 (6-2)	1.89	1055				0.933	
Dark reactivity with O_3	1510	1.10	1240				0.900	
Furan	1000 (6-3)	0.19	1335				0.751	
1225 (6-2), furan injection	1130	0.18	1455				0.651	
6-3 to 6-4-76	0900 (6-4)	——	1402 (6-3)				1.092	
Dark reactivity with O_3			0750 (6-4)				0.880	
Pyrrole, O_3			0835				0.531	
0710 (6-4), pyrrole injection			0910				0.428	
			1005				0.344	
6-3 to 6-4-76	0915 (6-4)	4.93	1430 (6-3)				1.183	
Dark reactivity with O_3	1005	4.59	1530				1.170	
Thiophene, O_3	1135	4.35	1602				1.165	
0705 (6-4), thiophene injection			0745 (6-4)				0.847	
			1205				0.751	
			1355				0.742	
6-3 to 6-4-76			1348 (6-3)				0.666	
O_3 decay (dark)[c]			1552				0.660	
O_3			0755 (6-4)				0.573	
			1217				0.540	
6-3 to 6-4-76			1348 (6-3)				1.220	
O_3 decay (dark)[c]			1540				1.210	
O_3			0800 (6-4)				1.006	
			1228				0.992	
			1419				0.988	
6-8-76	0900	9.42	0901	1.612	0.454	2.066		
Ozone formation	1100	8.85	1056	1.480	0.470	1.950	——	
Thiophene	1220	7.46	1203	1.110	0.788	1.898	——	
0945	1355	5.65	1348	0.476	1.094	1.570	——	
	1530	4.80	1510	0.196	1.112	1.308	——	
6-8-76	0930	10.6	0935	0.440	0.124	0.564		
Ozone formation	1114	9.06	1045	0.466	0.004	0.470	——	
Thiophene	1245	6.51	1225	——	0.198	0.198	0.276	
0945	1435	4.04	1415	——	0.172	0.172	0.173	
	1655	3.73	1540	——	0.066	0.066	0.131	
6-8-76	0835	10.1	0911	——	——	——	——	
Light stability	1050	9.90	1055	——	0.012	0.012	0.010	
Thiophene	1235	9.56	1220	——	d	d	0.008	
0945	1350	9.16	1355	——	0.010	0.010	0.010	
	1525	9.14	1510	——	0.012	0.012	0.009	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
6-8-76 Ozone formation Furan 0945	0915	9.51	0914	1.606	0.436	2.042		
	1108	[e]—	1105	—	d	d	>1.4	
	1210	—	1210	—	0.606	0.606	>1.4	
			1415	—	0.384	0.384	>1.4	
			1530	—	0.264	0.264	>1.4	
6-8-76 NO oxidation (light)[c] NO, NO_2 0945			0925	1.626	0.474	2.100		
			1105	d	d	d	—	
			1230	1.602	0.458	2.060	—	
			1347	1.598	0.440	2.038	—	
			1520	d	d	d	—	
6-8-76 Clean air irradiation[c] Clean air 0945			0939	—	0.006	0.006		
			1050	—	—		—	
			1155	—	0.008	0.008	0.006	
			1405	—	0.016	0.016	0.012	
			1520	—	0.012	0.012	0.013	
6-9-76 Clean air irradiation[c] Clean air 1025			1019	—	0.010	0.010		
			1045	—	0.012	0.012	0.014	
			1240	—	0.040[e]	0.040[e]	0.028	
			1355	—	0.044[e]	0.044[e]	0.030	
			1501	—	0.058[e]	0.058[e]	0.034	
6-9-76 NO oxidation (light)[c] NO, NO_2 1025			1010	1.732	0.324	2.056		
			1045	1.688	0.350[e]	2.038[e]		
			1230	1.626	0.492[e]	2.118[e]	—	
			1328	1.596	0.512[e]	2.108[e]	—	
			1524	1.516	0.440	1.956	—	
6-9-76 Ozone formation Furan 0949	0830	10.6	0945	1.692	0.390	2.082		
	0840	10.8	1102	—	0.668[e]	0.668[e]	1.260	
	0910	10.3	1229	—	0.812	0.812	1.303	
	0950[e]	5.12	1328	—	0.686	0.686	1.215	
	1020	0.21	1514	—	0.414	0.414	1.126	
	1125	—						
6-9-76 Ozone formation Pyrrole 1002	0905	11.4	0954	1.700	0.282	1.982		
	1130	—	1102	—	0.524[e]	0.524[e]	0.305	
			1216	—	0.358[e]	0.358[e]	0.272	
			1350	—	0.468	0.468	0.286	
			1501	—	0.320	0.320	0.268	
6-9-76 Ozone formation Pyrrole 1025	0930	10.4	1015	0.408	0.080	0.488		
	1110	—	1055	—	0.068	0.068	0.310	
	1140	—	1240	—	0.070	0.070	0.385	
			1355	—	0.076	0.076	0.371	
			1514	—	0.058	0.058	0.371	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
6-9-76	0920	11.1	1005	—	0.032	0.032		
Light stability	1105	9.90	1033	—	0.016	0.016	—	
Pyrrole	1230	9.66	1204	—	0.020	0.020	—	
1025	1405	8.84	1349	—	0.082	0.082	—	
	1550	8.04	1524	—	0.064	0.064	—	
6-10-76	0720	10.1	0710	1.154	0.264	1.418		
Ozone formation	0935	2.90	0926	—	0.804	0.804	0.523	
Furan			1100	—	0.372	0.372	0.928	
0820			1226	—	0.272	0.272	1.066	
			1350	—	0.170	0.170	1.013	
6-10-76	0725	10.8	0715	1.134	0.264	1.398		
Ozone formation	0940	—	0931	—	0.708	0.708	0.881	
2-Methylfuran		—	1103	—	0.676	0.676	0.876	
0820			1230	—	0.680	0.680	0.924	
			1353	—	0.590	0.590	0.925	
6-10-76	0730	10.8	0720	0.292	0.062	0.354		
Ozone formation	0945	3.18	0936	—	0.240^{e}	0.240^{e}	0.046	
2-Methylfuran	1245	0.73	1110	—	0.212	0.212	0.029	
0820	1425	0.28	1238	—	0.240^{e}	0.240^{e}	0.065	
			1359	—	0.190	0.190	0.088	
6-10-76	0815	15.9	0755	1.114	0.318	1.432		
Ozone formation	1025	—	1013	—	0.928	0.928	0.673	
2,5-Dimethylfuran		—	1137	—	0.826	0.826	0.716	
0820			1306	—	0.796	0.796	0.816	
			1423	—	0.802	0.802	0.841	
6-10-76	0820	10.4	0759	0.290	0.062	0.352		
Ozone formation	1030	0.09	1017	—	0.240^{e}	0.240^{e}	0.026	
2,5-Dimethylfuran			1141	—	0.248^{e}	0.248^{e}	0.129	
0820			1308	—	0.246^{e}	0.246^{e}	0.240	
			1428	—	0.286^{e}	0.286^{e}	0.297	
6-10-76	0735	10.1	0727	1.108	0.274	1.382		
Ozone formation	1005	9.71	0948	0.994	0.366	1.360	—	
Thiophene	1250	5.88	1115	0.556	0.712	1.268	—	
0820	1430	4.25	1240	—	0.944	0.944	0.100	
			1404	—	0.576	0.576	0.256	
6-10-76	0740	10.1	0734	1.184	0.270	1.454		
Ozone formation	0955	8.92	0946	0.800	0.588	1.388	—	
2-Methylthiophene	1255	1.52	1120	—	0.824	0.824	0.176	
0820	1440	1.00	1245	—	0.602	0.602	0.391	
			1407	—	0.538	0.538	0.347	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analysos, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
6-10-76	0750	18.6	0740	0.316	0.080	0.396		
Ozone formation	1007	11.5	0953	—	0.210	0.210	0.094	
2-Methylthiophene	1450	0.44	1125	—	0.128	0.128	0.044	
0820			1253	—	0.120	0.120	0.021	
			1411	—	0.094	0.094	0.013	
6-10-76	0800	12.2	0750	1.186	0.316	1.502		
Ozone formation	1020	—	1004	—	0.394	0.394	0.598	
Pyrrole			1133	—	0.348	0.348	0.627	
0820			1301	—	0.224	0.224	0.614	
			1419	—	0.170	0.170	0.574	
6-17 to 6-18-76	0925 (6-17)	9.37	0927	0.004	1.166[e]	1.170[e]		
Dark reactivity with NO_x	1025	d	(6-17)					
Pyrrole, NO_2	1220	8.81	1156	0.004	1.162	1.166		
	1415	8.45	1305	d	d	d		
			1358	0.004	1.026	1.030		
			1455	0.004	1.022	1.026		
			0745	0.014	0.892	0.906		
			(6-18)					
6-17 to 6-18-76	0915 (6-17)	8.81	0912	—	0.958	0.958		
Dark reactivity with NO_x	1035	8.76	(6-17)					
Thiophene, NO_2	1200	8.71	1149	—	0.932[e]	0.932[e]		
	1415	8.69	1250	—	0.924[e]	0.924[e]		
			1345	—	0.912[e]	0.912[e]		
			0733	—	0.772	0.772		
			(6-18)					
6-17 to 6-18-76	0900	10.2	0903	—	d	d		
Dark reactivity with NO_x	1025	10.3	(6-17)					
Furan, NO_2	1235	10.3	1153	—	1.182	1.182		
	1430	9.99	1309	—	1.162	1.162		
			1402	—	1.144	1.144		
			1441	—	1.111	1.111		
			0755	—	0.508	0.508		
			(6-18)					
6-17 to 6-18-76			0800	—	0.980[e]	0.980[e]		
Dark reactivity with NO_x			(6-17)					
NO_2 (no added hydrocarbon)			1025	—	0.986	0.986		
			1349	—	0.948	0.948		
			1433	—	0.930	0.930		
			0750	—	0.748	0.748		
			(6-18)					

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
6-17 to 6-18-76 NO oxidation (dark)[c] NO			0810 (6-17)	d	d	d		
			1144	1.062	0.060	1.122		
			1300	1.028	0.076	1.104		
			1354	1.002	0.091	1.093		
			1450	0.972	0.096	1.068		
			0741 (6-18)	0.670	0.242	0.912		
6-22-76 Ozone formation Toluene 0925	0835	12.0	0847	1.648	0.388	2.036		
	1240	10.9	1049	1.276^{f}	0.390^{f}	1.666^{f}	—	
	1435	8.77	1217	1.212^{f}	0.486^{f}	1.698^{f}	—	
			1329	1.092^{f}	0.560^{f}	1.652^{f}	—	
			1437	0.592^{f}	0.412^{f}	1.004^{f}	—	
6-22-76 Ozone formation Toluene 0925	0850	11.2	0854	0.376	0.096	0.472		
	1215	8.83	1054	0.028^{f}	0.310^{f}	0.338^{f}	0.051	
	1500	7.16	1224	—^{f}	0.110^{f}	0.110^{f}	0.343	
			1338	—^{f}	0.060^{f}	0.060^{f}	0.338	
			1442	—^{f}	0.062^{f}	0.062^{f}	0.259	
6-22-76 Ozone formation Ethylbenzene 0925	0905	11.9	0915	1.832	0.472	2.304		
	1350	9.45	1059	1.542^{f}	0.440^{f}	1.982^{f}	—	
	1550	9.39	1233	1.472^{f}	0.440^{f}	1.912^{f}	—	
			1342	1.434^{f}	0.478^{f}	1.912^{f}	—	
			1453	0.906^{f}	0.320^{f}	1.226^{f}	—	
6-22-76 Ozone formation Ethylbenzene 0925	0915	11.4	0920	0.462	0.172	0.634		
	1305	7.99	1104	0.222^{f}	0.238^{f}	0.460^{f}	0.006	
	1510	5.56	1243	0.014^{f}	0.334^{f}	0.348^{f}	0.060	
			1346	—^{f}	0.216^{f}	0.216^{f}	0.268	
			1459	—^{f}	0.080^{f}	0.080^{f}	0.313	
6-29-76 Ozone formation Thiophene 1002	0855	9.48	0858	1.570	0.462	2.032		0.020
	1145	8.39	1113	1.040^{f}	0.436^{f}	1.476^{f}	—	0.061
	1405	4.83	1303	0.100^{f}	0.162^{f}	0.262^{f}	—	0.224
	1615	3.27	1503	0.006^{f}	0.162^{f}	0.168^{f}	0.013	0.409
6-29-76 Ozone formation Thiophene 1002	0905	7.83	0905	0.394	0.110	0.504		0.000
	1200	3.76	1100	0.012^{f}	0.236^{f}	0.248^{f}	0.060	0.178
	1415	2.14	1314	—^{f}	0.046^{f}	0.046^{f}	0.060	0.312
	1625	1.66	1515	—^{f}	0.016^{f}	0.016^{f}	0.056	0.426
6-29-76 Ozone formation 2-Methylthiophene 1002	0910	[illegible].91	0912	1.570	0.473	2.043		0.016
	1220	3.11	1125	0.554^{f}	0.814^{f}	1.368^{f}	—	0.266
	1425	—	1318	—^{f}	0.724^{f}	0.724^{f}	0.333	0.766
			1527	—^{f}	0.064^{f}	0.061^{f}	0.246	0.575

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[C_3] ppm	[SO_2] ppm
6-29-76	0920	12.0	0916	0.506	0.154	0.660		0.000
Ozone formation	1150	4.93	1136	—^{f}	0.032^f	0.032^f	0.023	0.375
2-Methylthiophene	1435	2.36	1334	—^{f}	0.030^f	0.030^f	0.033	0.497
1002	1625	1.26	1539	—^{f}	0.028^f	0.028^f	0.038	0.591
6-29-76	0925	9.36	0927	1.608	0.518	2.126		0.018
Ozone formation	1210	2.35	1148	—^{f}	0.028^f	0.028^f	0.135	0.90
CH_3SCH_3	1440	1.82	1336	—^{f}	0.110^f	0.110^f	0.327	1.56
1002	1635	1.64	1552	—^{f}	0.028^f	0.028^f	0.073	0.99
6-29-76	0930	10.7	0923	0.392	0.128	0.520		0.000
Ozone formation	1225	6.51	1200	—^{f}	0.014^f	0.014^f	0.086	0.439
CH_3SCH_3	1455	5.44	1343	—^{f}	0.020^f	0.020^f	0.057	0.480
1002	1645	5.44	1604	—^{f}	0.014^f	0.014^f	0.034	0.520
6-29-76	0950	9.03	0954	1.866	0.522	2.388		0.006
Ozone formation	1240	—	1212	0.012^f	0.196^f	0.208^f	0.013	0.182
$(CH_3S)_2$	1505	—	1404	—^{f}	0.076^f	0.076^f	0.101	1.78
1002			1616	—^{f}	0.020^f	0.020^f	0.180	1.68
6-29-76	0940	11.0	0938	0.404	0.094	0.498		0.000
Ozone formation	1250	—	1223	—^{f}	0.016^f	0.016^f	0.241	0.272
$(CH_3S)_2$	1530	—	1417	—^{f}	0.016^f	0.016^f	0.195	2.70
1002			1628	—^{f}	0.016^f	0.016^f	0.146	2.56
7-1-76	0855	8.71	0836	1.696	0.492	2.188		0.014
Ozone formation	1035	6.78	1016	0.318^f	0.114^f	0.432^f	—	0.079
CH_3SH	1245	2.74	1217	0.224^f	0.154^f	0.378^f	—	0.445
0945	1450	1.28	1415	0.192^f	0.172^f	0.364^f	—	0.928
7-1-76	0905	11.2	0842	0.444	0.108	0.552		
Ozone formation	1045	9.07	1028	0.072^f	0.032^f	0.104^f	—	0.042
CH_3SH	1300	6.81	1227	0.036^f	0.048^f	0.084^f	0.001	0.243
0945	1440	3.86	1420	d	d	d	0.005	0.824
7-1-76	0915	10.2	0831	1.684	0.456	2.140		
Ozone formation	1100	1.42	1103	—^{f}	0.032^f	0.032^f	0.261	0.855
CH_3SCH_3	1310	1.01	1308	—^{f}	0.028^f	0.028^f	0.173	0.904
0945	1520	0.92	1453	—^{f}	0.028^f	0.028^f	0.136	0.926
7-1-76	0910	11.1	0825	—	0.004	0.004		
Light stability	1115	10.6	1053	—^{f}	0.004^f	0.004^f	0.003	0.017
CH_3SCH_3	1320	10.6	1254	—^{f}	0.012^f	0.012^f	0.006	0.044
0945	1500	10.3	1440	—^{f}	0.012^f	0.012^f	0.001	0.043

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
7-1-76	0945	12.1	0906	1.960	0.496[f]	2.456[f]		
Ozone formation	1140	—	1115	—[f]	0.244[f]	0.244[f]	0.055	2.13
$(CH_3S)_2$			1357	—[f]	0.046[f]	0.046[f]	0.212	2.09
0945			1555	—[f]	0.042[f]	0.042[f]	0.165	1.87
7-1-76	0925	12.0	0856	—	0.008[f]	0.008[f]		
Light stability	1125	7.58	1145	—[f]	0.002[f]	0.002[f]	—	1.23
$(CH_3S)_2$	1330	4.76	1333	—[f]	0.012[f]	0.012[f]	—	1.97
0945	1510	3.42	1509	—[f]	0.014[f]	0.014[f]	—	2.39
7-1-76		(10.0)[g]	0846	1.712[f]	0.512[f]	2.224[f]		
Ozone formation			1039	0.324[f]	0.108[f]	0.432[f]	—	0.025
COS			1241	0.292[f]	0.102[f]	0.394[f]	—	0.040
0945			1430	0.200[f]	0.078[f]	0.278[f]	—	0.045
7-1-76		(10.0)[g]	0852	0.430[f]	0.128[f]	0.558[f]		0.006
Ozone formation			1135	0.056[f]	0.030[f]	0.086[f]	—	0.022
COS			1321	0.056[f]	0.032[f]	0.088[f]	—	0.021
0945			1523	0.048[f]	0.032[f]	0.080[f]	—	0.019
7-16-76	0955	10.7	0954	1.606	0.720	2.326		
Ozone formation	1325	2.17	1237	—	0.628	0.628	1.596	
Cyclopentadiene			1501	—	0.538	0.538	1.499	
1035								
7-16-76	1005	11.5	1001	0.052	0.118[f]	0.620[f]		
Ozone formation	1310	—	1250	—[f]	0.118[f]	0.118[f]	0.622	
Cyclopentadiene			1354	—[f]	0.064[f]	0.064[f]	0.556	
1035			1518	—[f]	0.064[f]	0.064[f]	0.540	
7-23-76	0850	10.4	0819	1.920[f]	0.530[f]	2.450[f]		
Ozone formation	1110	6.9	1054	0.392[f]	1.770[f]	2.162[f]	—	
m-Xylene	1520	4.0	1242	—[f]	1.032[f]	1.032[f]	0.852	
0920			1443	—[f]	1.038[f]	1.038[f]	1.008	
7-23-76	0840	10.1	0813	0.466	0.126[f]	0.592[f]		
Ozone formation	1120	5.1	1048	—[f]	0.284[f]	0.284[f]	0.569	
m-Xylene	1355	3.7	1255	—[f]	0.232[f]	0.232[f]	0.481	
0920	1535	2.0	1448	d	d	d	0.441	
7-23-76	0900	10.1	0830	1.814[f]	0.552[f]	2.366		
Ozone formation	1130	9.2	1103	1.768[f]	0.552[f]	2.320[f]	—	
p-Xylene	1405	8.7	1322	1.668[f]	0.534[f]	2.202[f]	—	
0920	1550	8.7	1453	1.612[f]	0.630[f]	2.242[f]	—	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
7-23-76	0910	9.9	0824	0.472[f]	0.124[f]	0.596[f]		
Ozone formation	1215	6.8	1058	0.064[f]	0.466[f]	0.530[f]	—	
p-Xylene	1435	4.7	1409	—[f]	0.162[f]	0.162[f]	0.594	
0920	1600	5.1	1517	—[f]	0.278[f]	0.278[f]	0.532	
7-23-76	0825	10.3	0808	1.786[f]	0.494[f]	2.280[f]		
Ozone formation	1210	8.1	1041	1.628[f]	0.602[f]	2.230[f]		
o-Xylene	1425	4.5	1405	—[f]	1.198[f]	1.198[f]	0.385	
0920	1610	3.9	1508	—[f]	1.170[f]	1.170[f]	0.212	
7-23-76	0835	9.9	0802	0.438[f]	0.112[f]	0.550[f]		
Ozone formation	1100	7.1	1035	—[f]	0.380[f]	0.380[f]	0.281	
o-Xylene	1345	4.7	1230	—[f]	0.232[f]	0.232[f]	0.521	
0920	1510	4.0	1437	—[f]	0.212[f]	0.212[f]	0.501	
7-28-76		(5.0)[g]	0500	0.917	0.198	1.115		
Ozone formation			0755	0.863	0.240	1.103	—	
CH_3SH			0845				—	0.045
0500			0945	0.775	0.302	1.077	—	
			1045				—	0.150
			1145	0.605	0.410	1.015	—	
			1245				—	0.400
			1345	0.330	0.580	0.910	—	
			1445				—	0.720
			1545	0.020	0.700	0.720	0.015	
7-28-76		(5.0)[g]	0504	0.905	0.220	1.125		
Ozone formation			0755	0.695	0.385	1.080	—	
$(CH_3S)_2$			0855				0.225	1.40
0504			0955	0.018[e]	0.125[e]	0.143[e]	0.545	
			1055				0.594	1.35
			1155	d	d	d	0.568	
			1255				0.532	1.30
			1355	—	0.160[e]	0.160[e]	0.490	
			1455				0.443	1.27
			1555	—	0.265[e]	0.265[e]	0.410	
7-28-76		(5.0)[g]	0508	0.912[e]	0.208[e]	1.120[e]		
Ozone formation			0755	—	0.510	0.510	0.320	
CH_3SCH_3			0855				0.580	0.53
0508			0955	—	0.060[e]	0.060[e]	0.563	
			1055				0.514	0.55
			1155	—	0.042[e]	0.042[e]	0.458	
			1255				0.405	0.55
			1355	—	d	d	0.363	
			1455				0.325	0.54
			1555	—	0.080[e]	0.080[e]	0.295	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
7-28-76 Ozone formation C_3H_6 0455		(5.0)[g]	0455	0.920	0.215	1.135		
			0750	0.738	0.374	1.112	—	
			0850				—	—
			0950	0.005	0.950	0.955	0.075	
			1050				0.509	—
			1150	d	0.590	0.610	0.852	
			1250				0.945	—
			1350	—	0.450	0.450	0.941	
			1450				0.911	—
			1550	—	0.363	0.363	0.863	
8-5-76 Dark reactivity with O_3 CH_3SH, O_3 0709	0920	d	0923				1.101	
	1100	6.38	1102				1.033	
	1220	7.12	1225				0.970	
	1350	8.93	1353				0.901	
	1540	8.39	1537				0.826	
8-5-76 Dark stability CH_3SH 0751	1000	8.16						
	1120	9.72						
	1250	9.74						
	1435	8.71						
	1600	9.33						
8-5-76 Dark reactivity with O_3 CH_3SCH_3 0657	1050	9.44	0928				0.900	
	1230	9.93	1052				0.804	
	1400	9.56	1231				0.757	
	1545	9.99	1400				0.693	
			1542				0.620	
8-5-76 Dark stability CH_3SCH_3 0746	1005	11.4						
	1445	10.9						
8-5-76 Ozone decay (dark)[c] O_3 0607			0803				1.258	
			1115				1.228	
8-5-76 Dark reactivity with O_3 $(CH_3S)_2$ 0706	0940	13.5	0937				1.119	
	1105	12.4	1112				1.075	
	1240	12.2	1235				1.036	
	1430	12.8	1402				0.999	
	1555	12.8	1546				0.957	
8-5-76 Dark stability $(CH_3S)_2$ 0740	1015	12.3						
	1455	11.8						

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
8-6-76	0825	7.59	0806	0.893	0.202	1.095	—	
Dark reactivity with NO_x	0955	8.52	0942	0.854	0.230	1.084	—	
CH_3SH, NO, NO_2	1200	7.51	1146	0.820	0.235	1.055		
0720	1350	7.80	1347	0.823[e]	0.254[e]	1.077[e]		
	1555	7.67	1543	0.802[e]	0.279[e]	1.081[e]		
8-6-76	0815	11.1	0743	0.926	0.233	1.159	—	
Dark reactivity with NO_x	0945	11.2	0925	0.903	0.260	1.163	—	
CH_3SCH_3, NO, NO_2	1140	11.1	1136	0.839	0.281	1.120		
0647	1335	11.1	1330	0.832[e]	0.297[e]	1.129[e]		
	1540	11.1	1537	0.820[e]	0.327[e]	1.147[e]		
8-6-76	0835	15.6	0755	0.875	0.239	1.114	—	
Dark reactivity with NO_x	0935	14.5	0925	0.858	0.267	1.125	—	
$(CH_3S)_2$, NO, NO_2	1145	14.8	1140	0.791	0.270	1.061		
0655	1345	13.6	1341	0.763[e]	0.277[e]	1.040[e]		
8-6-76		(10.0)[g]	0810	0.882	0.224	1.106	—	
Dark reactivity with NO_x			0952	0.845	0.243	1.088	—	
COS, NO, NO_2			1152	0.809	0.263	1.072		
0727			1354	0.811[e]	0.294[e]	1.105[e]		
			1549	0.797[e]	0.317[e]	1.114[e]		
8-6-76			0746	0.943	0.223	1.166	—	
NO oxidation (dark)[c]			1156	0.869	0.271	1.140		
NO, NO_2			1456	0.848[e]	0.317[e]	1.165[e]		
0714								
8-11-76		(5.0)[g]	0040	0.730	0.150	0.880		
Ozone formation	0935	—	0845	0.622	0.220	0.882	—	
CH_3SH			0950	0.590	0.303	0.893		
0040			1140	0.450	0.435	0.885	—	
			1340	0.294	0.440	0.734	—	
			1440	0.145	0.531	0.676	—	
8-11-76		(5.0)[g]	0140	0.720	0.150	0.870		
Ozone formation	0925	1.08	0758	—	0.290[e]	0.290[e]	0.439	
CH_3SCH_3	1300	0.72	0855	—	d	d	0.495	
0140			1050	—	0.332[e]	0.332[e]	0.380	
			1150	—	0.355[e]	0.355[e]	0.362	
			1350	—	0.245[e]	0.245[e]	0.290	
			1450	—	0.278[e]	0.278[e]	0.260[e]	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
8-11-76		(5.0)[g]	0045	0.720	0.140	0.860		
Ozone formation	0940		0720	0.298	0.487	0.785	—	
$(CH_3S)_2$			0940	0.004	0.242	0.246	0.657	
0045			1041	—	0.122[e]	0.122[e]	0.655	
			1140	—	d	d	0.590	
			1342	—	0.120	0.120	0.505	
			1440	—	0.070	0.070	0.471	
8-11-76		(5.0)[g]	0150	0.730	0.170	0.900		
Ozone formation	0915	3.4	0758	0.420	0.412	0.832	—	
C_3H_6			0855	0.022	0.775	0.797	—	
0150			1050	—	0.690[e]	0.690[e]	0.922	
			1150	—	0.698[e]	0.698[e]	1.010	
			1354	—	0.650	0.650	1.070	
			1450	—	0.520	0.520	1.050	
8-17-76	0500	4.38	0455	0.608	0.185	0.793		
Ozone formation	0905	4.12	0904	0.198	0.575	0.773	—	
C_3H_6	1040	1.55	1200	—	0.522	0.522	1.113	
0530			1400	—	0.482	0.482	1.058	
			1655	—	0.418	0.418	1.018	
			1850	—	0.400	0.400	0.973	
8-17-76	0530	5.70	0520	0.671	0.198	0.869		
Ozone formation	0910	0.52	0904	—	0.410	0.410	0.534	
Furan			1200	—	0.138	0.138	0.952	
0530			1400	—	0.120	0.120	0.925	
			1655	—	0.084	0.084	0.806	
			1850	—	0.063	0.063	0.743	
8-17-76	0520	7.47	0508	0.698	0.223	0.921		
Ozone formation	0900	7.18	0855	0.670	0.240	0.910	—	
Thiophene	1040	0.62	1145	0.595	0.255	0.850	—	
0530			1345	0.538	0.272	0.810	—	
			1645	0.464	0.278	0.742	—	
			1845	0.444	0.295	0.739	—	
8-17-76	0510	4.59	0500	0.653	0.162	0.815		
Ozone formation	0855		0855	—	0.170	0.170	0.197	
Pyrrole			1145	—	0.097	0.097	0.247	
0530			1345	—	0.070	0.070	0.284	
			1645	—	0.038	0.038	0.290	
			1845	—	0.028	0.028	0.280	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppm C	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
8-19-76	0545	25.1	0511	1.290	0.300	1.590		
Ozone formation	0755	18.4	0750	—	1.376	1.376	0.214	
C_3H_6	1000	2.38	0950	—	1.336	1.336	0.601	
0511	1205	0.76	1207	—	1.274	1.274	0.465	
			1358	—	1.225	1.225	0.630	
8-19-76	0540	8.55	0505	1.318	0.320	1.638		
Ozone formation	0745	7.82	0745	0.980	0.594	1.574	—	
C_3H_6	0950	3.63	0950	—	1.240	1.240	0.298	
0505	1250	0.17	1150	—	1.068	1.068	1.470	
			1345	—	0.940	0.940	1.315	
			1545	—	0.872	0.872	d	
			1745	—	0.810	0.810	1.130	
			1950	—	0.780	0.780	1.023	
8-19-76	0515	9.0	0453	0.318	0.074	0.392		
Ozone formation	0805	8.5	0800	—	0.394	0.394	0.042	
C_3H_6	1015	2.65	1005	—	0.228^e	0.228^e	0.289	
0550	1210	1.61	1105	—	0.260	0.260	0.164	
			1400	—	0.240	0.240	0.190	
			1600	—	0.218	0.218	0.178	
			1745	—	0.215	0.215	0.160	
			2000	—	0.215	0.215	0.119	
8-19-76	0530	4.50	0459	0.652	0.152	0.804		
Ozone formation	0815	4.20	0805	0.490	0.318	0.808	—	
C_3H_6	1020	2.29	1010	—	0.672	0.672	0.254	
0459	1225	0.19	1215	—	0.595	0.595	1.002	
			1410	—	0.580	0.580	0.942	
			1615	—	0.540	0.540	0.870	
			1800	—	0.465^e	0.465^e	0.830	
			2015	—	0.492	0.492	0.772	
8-19-76	0545	4.75	0530	0.692	0.158	0.850		
Ozone formation	0820	4.46	0815	0.632	0.210	0.842	—	
CH_3SH	1005	3.97	1010	0.518	0.332	0.850	—	
0530	1225	1.74	1215	0.320	0.440	0.760	—	
			1410	—	0.555	0.555	0.037	
			1615	—	0.180	0.180	0.360	
8-19-76	0535	5.33	0518	0.692	0.158	0.850		
Ozone formation	0810	2.35	0805	—	0.346	0.346	0.332	
CH_3SCH_3	1015	0.79	1010	—	0.300	0.300	0.510	
0518	1155	0.71	1150	—	0.060^e	0.060^e	0.441	
			1345	—	0.090^e	0.090^e	0.335	
			1550	—	0.068^e	0.068^e	0.309	
			1745	—	0.055^e	0.055^e	0.274	
			1950	—	0.062^e	0.062^e	0.255	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppmC	Time of Analyses, EST	[NO] ppm	[NO_2] ppm	[NO_x] ppm	[O_3] ppm	[SO_2] ppm
8-19-76	0540	6.48	0524	0.664	0.166	0.830		
Ozone formation	0900	—	0805	—	0.626	0.626	0.074	
$(CH_3S)_2$			1015	—	0.384	0.384	0.844	
0524								
2-2 to 2-3-77								
O_3 decay[c]			1509 (2-2)				0.870	
O_3			2201				0.817	
			0810 (2-3)				0.740	
2-2 to 2-3-77								
O_3 decay[c]			1522 (2-2)				1.133	
O_3			2213				1.078	
			0824 (2-3)				0.990	
2-2 to 2-3-77								
O_3 decay[c]			1530 (2-2)				1.019	
O_3			2223				0.970	
			0839 (2-3)				0.879	
2-2 to 2-3-77								
O_3 decay[c]			1548 (2-2)				0.926	
O_3			2245				0.873	
			0904 (2-3)				0.787	
2-4-77	1055	4.79	1028				0.401	
Dark reactivity with O_3	1110	4.56	1055				0.228	
C_3H_6	1145	4.12	1104				0.193	
1043, C_3H_6 injection	1220	4.00	1111				0.164	
	1305	3.87	1215				0.034	
	1335	3.85	1226				0.024	
	1400	3.83	1258				0.012	
	1500	3.87	1307				0.009	
	1600	3.80						
2-4-77	0750	16.91	0703				0.898	
Dark reactivity with O_3	0845	15.59	0834				0.311	
Furan	0925	15.11	0850				0.245	
0717, furan injection	1005	14.83	0921				0.185	
	1115	14.42	0929				0.174	
	1155	14.32	0950				0.134	
	1255	14.20	1005				0.116	
	1310	13.99	1113				0.058	
	1340	14.06	1120				0.057	
	1420	14.06	1153				0.039	
	1520	14.10	1202				0.035	
	1620	13.99	1235				0.025	
			1255				0.020	
			1302				0.018	
			1313				0.016	

RESULTS OF BAG STUDIES

Test description[a]	Time of HC Analysis, EST	[HC] ppm C	Time of Analyses, EST	[NO] ppm	[NO$_2$] ppm	[NO$_x$] ppm	[O$_3$] ppm	[SO$_2$] ppm
2-4-77	0740	18.03	0643				0.798	
Dark reactivity with O$_3$	0855	17.77	0713				0.711	
Thiophene	0950	18.05	0747				0.642	
0701, thiophene injection	1130	17.68	0847				0.477	
	1205	17.50	0856				0.460	
	1245	17.48	0945				0.389	
			0954				0.385	
			1115				0.293	
			1131				0.287	
			1157				0.253	
			1208				0.238	
			1231				0.215	
			1245				0.202	
2-4-77	1030	8.98	1012				0.509	
Dark reactivity with O$_3$	1100	7.26	1039				0.150	
Pyrrole	1140	6.48	1102				0.055	
1030, pyrrole injection	1215	6.80	1108				0.043	
	1230	6.58	1134				0.012	
	1325	6.39	1142				0.008	
	1350	7.07	1212				0.002	
	1440	7.35	1222				0.001	
	1540	6.42						
	1635	6.58						

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[a] The test description follows this format: date, type of experiment, test compound, and time of initial exposure, EST.

[b] Entries denoted by blanks represent nondetected concentrations.

[c] Bag characterization experiment.

[d] Data discarded.

[e] Data questionable.

[f] Data questionable due to sampling line losses.

[g] Target initial condition, analysis not available.

APPENDIX C

Hydrocarbon Analyses From Chamber Runs

Appendix C. HYDROCARBON ANALYSES FROM CHAMBER RUNS

			DAY 1				DAY 2	
Hydrocarbon	Date	Chamber	Time[a]	[HC][b]	Time	[HC]	Time	[HC]
Furan	7/13-15/76[c]	1	0432	4.72	1225	ND[d]	0430	ND
Thiophene		2	0440	4.01	1235	1.79	0440	0.52
Pyrrole		3	0448	2.94	1245	ND	0450	ND
Propylene		4	0456	5.16	1255	ND	0500	ND
Furan	8/17-19/76[c]	1	0436	4.90	0920	ND		
Thiophene		2	0445	11.9	0910	0.77		
Pyrrole		3	0453	ND[e]	0900	ND		
Propylene		4	0504	5.23	0850	3.67		
Furan	7/20-22/76[f]	1	0430	5.03	1250	ND		
Thiophene		2	0440	5.54	1300	0.79		
Pyrrole		3	0450	ND[e]	1310	ND		
Propylene		4	0500	4.96	1320	ND		
Methanethiol	7/28-30/76[c]	1	0430	ND				
Methyl disulfide		2	0440	ND				
Methyl sulfide		3	0450	5.81				
Propylene		4	0500	5.22				
Methanethiol	8/10-13/76[f]	1	0530	ND[g]	1440	ND		
Methyl disulfide		2	0535	7.17	1450	ND		
Methyl sulfide		3	0540	5.24	1500	ND		
Propylene		4	0545	4.14	1510	ND		

[a] Time of sample collection, EST.

[b] Concentration of hydrocarbon, ppmC.

[c] Static run.

[d] ND = not detected.

[e] Pyrrole peak could not be clearly resolved.

[f] Dilution run.

[g] Compound detected with a retention time similar to methyl disulfide at a concentration of 3.81 ppmC.

APPENDIX D

Detailed Data Sheets

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-13-76
% POSSIBLE MINUTES SUNSHINE, 93
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.003	0.013	0.005	0.018					0.0	0.0				
1.13	0.003	0.010	0.007	0.017					0.0	0.0	22.22			
2.13	0.003	0.008	0.007	0.015					0.0	0.0				
3.13	0.003	0.019	0.144	0.163					0.0	0.0				
4.13	0.003	0.797	0.217	1.014					0.0	0.0	18.33			
5.13	0.002	0.794	0.213	1.007					0.05	0.40				
6.13	0.0	0.760	0.213	0.973					0.22	4.76				
7.13	0.0	0.697	0.268	0.965					0.37	19.16	20.00			
8.13	0.0	0.333	0.539	0.872					0.67	43.76				
9.13	0.746	0.0	0.257	0.257					0.92	85.96				
10.13	0.701	0.0	0.155	0.155		0.842	0.037	0.008	1.20	143.40	24.44			
11.13	0.657	0.0	0.119	0.119					1.45	217.40				
12.13	0.613	0.0	0.093	0.093					1.40	304.00				
13.13	0.565	0.0	0.074	0.074					1.29	387.12	28.33			
14.13	0.515	0.0	0.062	0.062					1.15	463.40				
15.13	0.473	0.0	0.053	0.053					0.98	531.04				
16.13	0.437	0.0	0.047	0.047		0.829	0.034	0.021	0.74	587.92	31.06			
17.13	0.405	0.0	0.043	0.043					0.41	629.68				
18.13	0.378	0.0	0.037	0.037					0.15	652.20				
19.13	0.352	0.0	0.030	0.030					0.02	660.16	28.33			
20.13	0.331	0.0	0.027	0.027					0.0	661.20				
21.13	0.315	0.0	0.023	0.023					0.0	661.20				
22.13	0.300	0.0	0.018	0.018					0.0	661.20	22.78			
23.13	0.288	0.0	0.017	0.017					0.0	661.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1,   FURAN   , 0% DILUTION

DAY 2, 7-14-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.276	0.0	0.016	0.016					0.0	0.0				
1.13	0.267	0.0	0.015	0.015					0.0	0.0	17.78			
2.13	0.259	0.0	0.015	0.015					0.0	0.0				
3.13	0.251	0.0	0.015	0.015					0.0	0.0				
4.13	0.243	0.0	0.015	0.015					0.0	0.0	17.78			
5.13	0.235	0.0	0.014	0.014					0.04	0.32				
6.13	0.223	0.0	0.015	0.015					0.16	3.68				
7.13	0.206	0.0	0.015	0.015					0.46	15.68	17.22			
8.13	0.187	0.0	0.018	0.018					0.82	46.16				
9.13	0.175	0.0	0.023	0.023					1.08	97.44				
10.13	0.174	0.0	0.024	0.024		0.183	0.011	0.039	1.17	162.96	27.22			
11.13	0.173	0.0	0.022	0.022					1.09	232.52				
12.13	0.186	0.0	0.022	0.022					1.13	298.24				
13.13	0.190	0.0	0.019	0.019					0.98	364.84	29.44			
14.13	0.192	0.0	0.019	0.019					0.99	423.72				
15.13	0.194	0.0	0.018	0.018					0.83	481.84				
16.13	0.190	0.0	0.018	0.018		0.166	0.011	0.017	0.44	528.52	30.56			
17.13	0.180	0.0	0.017	0.017					0.28	553.64				
18.13	0.172	0.0	0.016	0.016					0.12	569.16				
19.13	0.163	0.0	0.016	0.016					0.01	575.48	26.67			
20.13	0.155	0.0	0.014	0.014					0.0	576.00				
21.13	0.149	0.0	0.012	0.012					0.0	576.00				
22.13	0.144	0.0	0.012	0.012					0.0	576.00	22.22			
23.13	0.137	0.0	0.012	0.012					0.0	576.00				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 0% DILUTION

DAY 3, 7-15-76
% POSSIBLE MINUTES SUNSHINE, 76
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.132	0.0	0.012	0.012					0.0	0.0				
1.13	0.127	0.0	0.012	0.012					0.0	0.0	21.11			
2.13	0.121	0.0	0.011	0.011					0.0	0.0				
3.13	0.114	0.0	0.012	0.012					0.0	0.0				
4.13	0.109	0.0	0.012	0.012					0.0	0.0	20.00			
5.13	0.102	0.0	0.011	0.011					0.04	0.32				
6.13	0.095	0.0	0.012	0.012					0.23	4.24				
7.13	0.088	0.0	0.012	0.012					0.42	19.56	22.22			
8.13	0.085	0.0	0.013	0.013					0.76	47.48				
9.13	0.095	0.0	0.014	0.014					0.97	94.76				
10.13	0.111	0.0	0.012	0.012		0.283	0.017	0.128	1.12	154.16	31.11			
11.13	0.130	0.0	0.012	0.012					1.22	222.16				
12.13	0.145	0.0	0.012	0.012		0.239	0.017	0.146	1.27	295.76				
13.13	0.155	0.0	0.012	0.012					0.90	369.00	36.11			
14.13	0.160	0.0	0.012	0.012					0.78	422.04				
15.13	0.162	0.0	0.012	0.012					0.74	468.52				
16.13		0.0	0.012	0.012		0.234	0.014		0.50	511.00	36.11			
17.13									0.10	537.80				
18.13									0.01	543.08				
19.13									0.0	543.60	28.89			
20.13									0.0	543.60				
21.13									0.0	543.60				
22.13									0.0	543.60	23.89			
23.13									0.0	543.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2,   THIOPHENE   , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

PAGE 1

DAY 1, 7-13-76
% POSSIBLE MINUTES SUNSHINE, 93
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.005	0.013	0.006	0.019	0.0				0.0	0.0				
1.30	0.004	0.008	0.007	0.015	0.0				0.0	0.0	22.22			
2.30	0.003	0.005	0.007	0.012	0.0				0.0	0.0				
3.30	0.002	0.021	0.213	0.234	0.0				0.0	0.0				
4.30	0.001	0.816	0.213	1.029	0.0				0.0	0.0	18.33			
5.30	0.0	0.804	0.219	1.023	0.0				0.05	0.90				
6.30	0.0	0.778	0.211	0.989	0.0				0.22	6.96				
7.30	0.0	0.731	0.227	0.958	0.0				0.37	22.86	20.00			
8.30	0.0	0.705	0.251	0.956	0.010				0.67	50.46				
9.30	0.0	0.596	0.321	0.917	0.020				0.92	95.16				
10.30	0.001	0.418	0.385	0.803	0.040	0.009	0.384	0.043	1.20	155.40	24.44			
11.30	0.004	0.305	0.424	0.729	0.075				1.45	231.90				
12.30	0.010	0.196	0.413	0.609	0.115				1.40	318.00				
13.30	0.018	0.132	0.380	0.512	0.130				1.29	400.02	28.33			
14.30	0.029	0.090	0.342	0.432	0.160				1.15	474.90				
15.30	0.040	0.066	0.300	0.366	0.175				0.98	540.84				
16.30	0.044	0.053	0.271	0.324	0.180	0.0[a]	0.318	0.011	0.74	595.32	30.56			
17.30	0.041	0.041	0.250	0.291	0.185				0.41	633.78				
18.30	0.025	0.030	0.240	0.270	0.180				0.15	653.70				
19.30	0.008	0.019	0.241	0.260	0.170				0.02	660.36	28.33			
20.30	0.0	0.011	0.246	0.257	0.135				0.0	661.20				
21.30	0.0	0.007	0.243	0.250	0.110				0.0	661.20				
22.30	0.0	0.006	0.239	0.245	0.085				0.0	661.20	22.78			
23.30	0.0	0.005	0.234	0.239	0.075				0.0	661.20				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 0% DILUTION

DAY 2, 7-1?-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.0	0.004	0.232	0.236	0.060				0.0	0.0				
1.30	0.0	0.004	0.226	0.230	0.050				0.0	0.0	17.78			
2.30	0.0	0.003	0.223	0.226	0.040				0.0	0.0				
3.30	0.0	0.003	0.222	0.225	0.030				0.0	0.0				
4.30	0.0	0.003	0.218	0.221	0.025				0.0	0.0	17.78			
5.30	0.003	0.006	0.214	0.220	0.020				0.04	0.72				
6.30	0.013	0.023	0.184	0.207	0.020				0.16	5.28				
7.30	0.016	0.032	0.148	0.180	0.025				0.46	20.28	17.22			
8.30	0.034	0.034	0.120	0.154	0.040				0.82	54.36				
9.30	0.063	0.022	0.107	0.129	0.055				1.08	108.24				
10.30	0.098	0.013	0.087	0.100	0.070	0.019[a]	0.077	0.016	1.17	174.66	27.22			
11.30	0.127	0.008	0.070	0.078	0.080				1.09	243.42				
12.30	0.150	0.006	0.055	0.061	0.085				1.13	309.54				
13.30	0.171	0.005	0.042	0.047	0.085				0.98	374.64	29.44			
14.30	0.193	0.004	0.031	0.035	0.090				0.99	433.62				
15.30	0.201	0.003	0.018	0.021	0.085				0.83	490.14				
16.30	0.199	0.002	0.017	0.019	0.080	0.015[a]	0.065	0.008	0.44	532.92	30.56			
17.30	0.180	0.001	0.023	0.024	0.075				0.28	556.44				
18.30	0.165	0.001	0.022	0.023	0.070				0.12	570.36				
19.30	0.147	0.0	0.020	0.020	0.060				0.01	575.58	26.67			
20.30	0.129	0.0	0.018	0.018	0.050				0.0	576.00				
21.30	0.110	0.0	0.016	0.016	0.035				0.0	576.00				
22.30	0.093	0.0	0.016	0.016	0.025				0.0	576.00	22.22			
23.30	0.078	0.0	0.016	0.016	0.015				0.0	576.00				

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[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 0% DILUTION

DAY 3, 7-15-76
% POSSIBLE MINUTES SUNSHINE, 76
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.066	0.0	0.017	0.017	0.010				0.0	0.0				
1.30	0.054	0.0	0.016	0.016	0.005				0.0	0.0	21.11			
2.30	0.045	0.0	0.016	0.016	0.002				0.0	0.0				
3.30	0.037	0.0	0.016	0.016	0.002				0.0	0.0				
4.30	0.029	0.0	0.017	0.017	0.0				0.0	0.0	20.00			
5.30	0.021	0.0	0.017	0.017	0.0				0.04	0.72				
6.30	0.015	0.0	0.017	0.017	0.0				0.23	6.54				
7.30	0.028	0.002	0.018	0.020	0.003				0.42	23.76	22.22			
8.30	0.054	0.002	0.018	0.020	0.010				0.76	55.08				
9.30	0.088	0.003	0.018	0.021	0.012	0.166	0.013	0.118	0.97	104.46				
10.30	0.116	0.0	0.015	0.015	0.015				1.12	165.36	31.11			
11.30	0.140	0.0	0.014	0.014	0.015				1.22	234.36				
12.30	0.159	0.0	0.014	0.014	0.020	0.178	0.005	0.149	1.27	308.46				
13.30	0.173	0.0	0.014	0.014	0.015				0.90	378.00	36.11			
14.30	0.178	0.0	0.013	0.013	0.010				0.78	429.84				
15.30	0.178	0.0	0.013	0.013	0.010				0.74	475.92				
16.30					0.010	0.197	0.003		0.50	516.00	36.11			
17.30									0.10	538.80				
18.30									0.01	543.18				
19.30									0.0	543.60	28.89			
20.30									0.0	543.60				
21.30									0.0	543.60				
22.30									0.0	543.60	23.89			
23.30									0.0	543.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 5, PYRROLE , 0% DILUTION

PAGE 1

TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-13-76

% POSSIBLE MINUTES SUNSHINE, 93

RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.001	0.014	0.005	.019					0.0	0.0				
1.47	0.001	0.007	0.006	0.013					0.0	0.0	22.22			
2.47	0.001	0.005	0.006	0.011					0.0	0.0				
3.47	0.0	0.023	0.201	0.224					0.0	0.0				
4.47	0.0	0.864	0.173	1.037					0.0	0.0	18.33			
5.47	0.0	0.842	0.190	1.032					0.05	1.40				
6.47	0.0	0.657	0.323	0.980					0.22	9.16				
7.47	0.029	0.066	0.740	0.806					0.37	26.56	20.00			
8.47	0.058	0.033	0.428	0.461					0.67	57.16				
9.47	0.041	0.053	0.362	0.415					0.92	104.36				
10.47	0.033	0.067	0.314	0.381		0.094	0.297	0.003	1.20	167.40	24.44			
11.47	0.029	0.072	0.274	0.346					1.45	246.40				
12.47	0.027	0.070	0.240	0.310					1.40	332.00				
13.47	0.026	0.066	0.214	0.280					1.29	412.92	28.33			
14.47	0.024	0.063	0.194	0.257					1.15	486.40				
15.47	0.022	0.061	0.178	0.239					0.98	550.64				
16.47	0.020	0.058	0.170	0.228		0.074	0.207	0.033	0.74	602.72	30.56			
17.47	0.015	0.054	0.164	0.218					0.41	637.88				
18.47	0.007	0.046	0.166	0.212					0.15	655.20				
19.47	0.003	0.041	0.167	0.208					0.02	660.56	28.33			
20.47	0.0	0.035	0.166	0.201					0.0	661.20				
21.47	0.0	0.031	0.166	0.197					0.0	661.20				
22.47	0.0	0.028	0.163	0.191					0.0	661.20	22.78			
23.47	0.0	0.028	0.162	0.190					0.0	661.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, PYRROLE , 0% DILUTION

DAY 2, 7-14-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.0	0.026	0.161	0.187					0.0	0.0				
1.47	0.0	0.025	0.155	0.180					0.0	0.0	17.78			
2.47	0.0	0.025	0.155	0.180					0.0	0.0				
3.47	0.0	0.025	0.153	0.178					0.0	0.0				
4.47	0.0	0.023	0.153	0.176					0.0	0.0	17.78			
5.47	0.003	0.025	0.146	0.171					0.04	1.12				
6.47	0.008	0.035	0.132	0.167					0.16	6.88				
7.47	0.013	0.045	0.116	0.161					0.46	24.88	17.22			
8.47	0.015	0.054	0.103	0.157					0.82	62.56				
9.47	0.020	0.051	0.098	0.149					1.08	119.04				
10.47	0.024	0.041	0.097	0.138		0.035	0.094	0.0	1.17	186.36	27.22			
11.47	0.029	0.035	0.093	0.128					1.09	254.32				
12.47	0.029	0.027	0.095	0.122					1.13	320.84				
13.47	0.039	0.024	0.086	0.110					0.98	384.44	29.44			
14.47	0.042	0.020	0.082	0.102					0.99	443.52				
15.47	0.043	0.015	0.080	0.095					0.83	498.44				
16.47	0.043	0.010	0.077	0.087		0.016	0.095	0.017	0.44	537.32	30.56			
17.47	0.043	0.009	0.075	0.084					0.28	559.24				
18.47	0.039	0.004	0.075	0.079					0.12	571.56				
19.47	0.032	0.001	0.075	0.076					0.01	575.68	26.67			
20.47	0.026	0.0	0.069	0.069					0.0	576.00				
21.47	0.020	0.0	0.065	0.063					0.0	576.00				
22.47	0.015	0.0	0.060	0.060					0.0	576.00	22.22			
23.47	0.011	0.0	0.056	0.056					0.0	576.00				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, PYRROLE , 0% DILUTION

DAY 3, 7-15-76
% POSSIBLE MINUTES SUNSHINE, 76
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.010	0.0	0.053	0.053					0.0	0.0				
1.47	0.007	0.0	0.052	0.052					0.0	0.0	21.11			
2.47	0.004	0.0	0.051	0.051					0.0	0.0				
3.47	0.003	0.0	0.050	0.050					0.0	0.0				
4.47	0.002	0.0	0.049	0.049					0.0	0.0	20.00			
5.47	0.004	0.0	0.047	0.047					0.04	1.12				
6.47	0.011	0.008	0.040	0.048					0.23	8.84				
7.47	0.029	0.008	0.038	0.046					0.42	27.96	22.22			
8.47	0.054	0.007	0.034	0.041					0.76	62.68				
9.47	0.084	0.004	0.032	0.036		0.190	0.026	0.072	0.97	114.16				
10.47	0.110	0.001	0.025	0.026					1.12	176.56	31.11			
11.47	0.141	0.0	0.021	0.021					1.22	246.56				
12.47	0.170	0.0	0.017	0.017		0.174	0.020	0.096	1.27	321.16				
13.47	0.190	0.0	0.014	0.014					0.90	387.00	36.11			
14.47	0.196	0.0	0.013	0.013					0.78	437.64				
15.47	0.195								0.74	483.32				
16.47						0.167	0.021		0.50	521.00	36.11			
17.47									0.10	539.80				
18.47									0.01	543.28				
19.47									0.0	543.60	28.89			
20.47									0.0	543.60				
21.47									0.0	543.60				
22.47									0.0	543.60	23.89			
23.47									0.0	543.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

PAGE 1

DAY 1, 7-13-76
% POSSIBLE MINUTES SUNSHINE, 93
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.003	0.013	0.006	0.019					0.0	0.0				
1.63	0.003	0.007	0.006	0.013					0.0	0.0	22.22			
2.63	0.003	0.005	0.006	0.011					0.0	0.0				
3.63	0.002	0.018	0.171	0.189					0.0	0.0				
4.63	0.001	0.349	0.175	0.524					0.0	0.0	18.33			
5.63	0.0	0.688	0.175	0.863					0.05	1.90				
6.63	0.0	0.638	0.222	0.860					0.22	11.36				
7.63	0.0	0.515	0.313	0.828					0.37	30.26	20.00			
8.63	0.017	0.089	0.658	0.747					0.67	63.86				
9.63	0.825	0.004	0.510	0.514					0.92	113.56				
10.63	0.991	0.004	0.380	0.384		1.321	0.053	0.186	1.20	179.40	24.44			
11.63	0.999	0.004	0.355	0.359					1.45	260.90				
12.63	1.090	0.001	0.326	0.327					1.40	346.00				
13.63	1.093	0.001	0.295	0.296					1.29	425.82	28.33			
14.63	1.117	0.0	0.263	0.263					1.15	497.90				
15.63	1.125	0.0	0.243	0.243					0.98	560.44				
16.63	1.098	0.0	0.218	0.218		1.201	0.044	0.137	0.74	610.12	30.56			
17.63	1.063	0.0	0.192	0.192					0.41	641.98				
18.63	1.009	0.0	0.169	0.169					0.15	656.70				
19.63	0.961	0.0	0.147	0.147					0.02	660.76	28.33			
20.63	0.922	0.0	0.134	0.134					0.0	661.20				
21.63	0.896	0.0	0.125	0.125					0.0	661.20				
22.63	0.875	0.0	0.118	0.118					0.0	661.20	22.78			
23.63	0.855	0.0	0.115	0.115					0.0	661.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION

DAY 2, 7-14-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.834	0.0	0.110	0.110					0.0	0.0				
1.63	0.817	0.0	0.108	0.108					0.0	0.0	17.78			
2.63	0.806	0.0	0.105	0.105					0.0	0.0				
3.63	0.790	0.0	0.103	0.103					0.0	0.0				
4.63	0.770	0.0	0.099	0.099					0.0	0.0	17.78			
5.63	0.765	0.0	0.098	0.098					0.04	1.52				
6.63	0.746	0.0	0.096	0.096					0.16	8.48				
7.63	0.730	0.0	0.097	0.097					0.46	29.48	17.22			
8.63	0.712	0.001	0.103	0.104					0.82	70.76				
9.63	0.699	0.002	0.106	0.108					1.08	129.84				
10.63	0.702	0.003	0.100	0.103		0.762	0.017	0.195	1.17	198.06	27.22			
11.63	0.707	0.003	0.094	0.097					1.09	265.22				
12.63	0.699	0.004	0.089	0.093					1.13	332.14				
13.63	0.702	0.004	0.086	0.090					0.98	394.24	29.44			
14.63	0.700	0.005	0.074	0.079					0.99	453.42				
15.63	0.688	0.004	0.067	0.071					0.83	506.74				
16.63	0.662	0.003	0.059	0.062		0.541	0.016		0.44	541.72	30.56			
17.63	0.633	0.002	0.053	0.055					0.28	562.04				
18.63	0.610	0.002	0.050	0.052					0.12	572.76				
19.63	0.591	0.002	0.045	0.047					0.01	575.78	26.67			
20.63	0.576	0.001	0.040	0.041					0.0	576.00				
21.63	0.560	0.0	0.037	0.037					0.0	576.00				
22.63	0.544	0.0	0.032	0.032					0.0	576.00	22.22			
23.63	0.531	0.0	0.032	0.032					0.0	576.00				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION

DAY 3, 7-15-76
% POSSIBLE MINUTES SUNSHINE, 76
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.515	0.0	0.030	0.030					0.0	0.0				
1.63	0.504	0.0	0.029	0.029					0.0	0.0	21.11			
2.63	0.492	0.0	0.029	0.029					0.0	0.0				
3.63	0.481	0.0	0.028	0.028					0.0	0.0				
4.63	0.471	0.0	0.028	0.028					0.0	0.0	20.00			
5.63	0.460	0.0	0.027	0.027					0.04	1.52				
6.63	0.450	0.001	0.028	0.029					0.23	11.14				
7.63	0.435	0.004	0.033	0.037					0.42	32.16	22.22			
8.63	0.428	0.006	0.034	0.040					0.76	70.28				
9.63	0.417	0.004	0.031	0.035		0.601	0.016	0.182	0.97	123.86				
10.63	0.402	0.003	0.031	0.034					1.12	187.76	31.11			
11.63	0.401	0.002	0.029	0.031					1.22	258.76				
12.63	0.399	0.001	0.027	0.028		0.519	0.014	0.126	1.27	333.86				
13.63	0.391	0.0	0.025	0.025					0.90	396.00	36.11			
14.63	0.375	0.0	0.023	0.023					0.78	445.44				
15.63	0.355	0.0	0.022	0.022					0.74	490.72				
16.63						0.527	0.017		0.50	526.00	36.11			
17.63									0.10	540.80				
18.63									0.01	543.38				
19.63									0.0	543.60	28.89			
20.63									0.0	543.60				
21.63									0.0	543.60				
22.63									0.0	543.60	23.89			
23.63									0.0	543.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-20-76
% POSSIBLE MINUTES SUNSHINE, 74
RDU AIRPORT MAXIMUM TEMPERATURE, 33.89 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.0	0.030	0.001	0.031					0.0	0.0				
1.13	0.0	0.030	0.001	0.031					0.0	0.0	21.11			
2.13	0.0	0.030	0.001	0.031					0.0	0.0				
3.13	0.0	0.035	0.082	0.117					0.0	0.0				
4.13	0.0	0.845	0.185	1.030					0.0	0.0	18.89			
5.13	0.0	0.800	0.200	1.000					0.03	0.24				
6.13	0.0	0.769	0.213	0.982					0.21	3.48				
7.13	0.0	0.722	0.265	0.987					0.46	18.08	21.11			
8.13	0.030	0.090	0.750	0.840					0.73	47.84		1.95	8.00	
9.13	0.650	0.006	0.230	0.236					1.00	93.80				
10.13	0.555	0.003	0.137	0.140		0.569		0.494	1.03	154.04	28.33			
11.13	0.450	0.007	0.090	0.097					1.14	216.72				
12.13	0.370	0.008	0.062	0.070					1.10	284.80				
13.13	0.300	0.007	0.044	0.051			0.019		1.24	351.92	31.67			
14.13	0.250	0.008	0.032	0.040					1.15	425.60				
15.13	0.208	0.009	0.024	0.033			0.011		0.92	492.76				
16.13	0.172	0.011	0.020	0.031					0.68	546.04	30.00			
17.13	0.141	0.012	0.015	0.027		0.422	0.015	0.340	0.32	583.96				
18.13	0.112	0.013	0.012	0.025					0.18	602.04				
19.13	0.089	0.017	0.012	0.029					0.03	611.64	27.78			
20.13	0.070	0.019	0.010	0.029			0.020		0.0	613.20				
21.13	0.055	0.020	0.010	0.030					0.0	613.20				
22.13	0.043	0.021	0.009	0.030					0.0	613.20	23.89			
23.13	0.035	0.023	0.009	0.032					0.0	613.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 95% DILUTION

DAY 2, 7-21-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.00 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.028	0.028	0.011	0.039					0.0	0.0				
1.13	0.022	0.026	0.007	0.033					0.0	0.0	22.78			
2.13	0.017	0.027	0.008	0.035			0.004		0.0	0.0				
3.13	0.011	0.027	0.007	0.034					0.0	0.0				
4.13	0.008	0.025	0.007	0.032					0.0	0.0	21.67			
5.13	0.004	0.026	0.007	0.033					0.03	0.24				
6.13	0.002	0.025	0.006	0.031					0.19	3.32				
7.13	0.002	0.026	0.006	0.032					0.42	16.56	21.67			
8.13	0.008	0.015	0.007	0.022					0.68	43.84		1.95		8.00
9.13	0.018	0.025	0.007	0.032					0.94	86.72				
10.13	0.030	0.027	0.008	0.035		0.024	0.008	0.289	1.04	143.92	30.00			
11.13	0.045	0.025	0.009	0.034					1.11	206.88				
12.13	0.061	0.021	0.009	0.030					1.24	274.52				
13.13	0.075	0.008	0.010	0.018					1.11	347.88	32.22			
14.13	0.088	0.017	0.010	0.027					0.96	413.28				
15.13	0.100	0.017	0.010	0.027					0.91	470.48				
16.13	0.108	0.014	0.011	0.025					0.65	523.00	33.33			
17.13	0.109	0.013	0.010	0.023		0.017	0.008		0.38	559.84				
18.13	0.105	0.010	0.010	0.020					0.13	580.64				
19.13	0.099	0.012	0.010	0.022					0.02	587.56	31.11			
20.13	0.093	0.012	0.010	0.022					0.0	588.60				
21.13	0.088	0.016	0.009	0.025					0.0	588.60				
22.13	0.084	0.019	0.009	0.028					0.0	588.60	25.56			
23.13	0.079	0.020	0.009	0.029					0.0	588.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 95% DILUTION

DAY 3, 7-22-76
% POSSIBLE MINUTES SUNSHINE, 69
RDU AIRPORT MAXIMUM TEMPERATURE, 36.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.075	0.025	0.008	0.033					0.0	0.0				
1.13	0.073	0.028	0.008	0.036					0.0	0.0	23.89			
2.13	0.068	0.030	0.008	0.038					0.0	0.0				
3.13	0.065	0.033	0.008	0.041					0.0	0.0				
4.13	0.060	0.034	0.009	0.042					0.0	0.0	22.78			
5.13	0.056	0.035	0.008	0.043					0.03	0.24				
6.13	0.050	0.032	0.008	0.040					0.20	3.40				
7.13	0.044	0.038	0.009	0.047					0.40	17.00	22.78			
8.13	0.045	0.038	0.010	0.048					0.68	43.24				
9.13	0.063	0.033	0.012	0.045		0.091	0.008	0.056	0.88	85.64				
10.13	0.089	0.030	0.012	0.042					1.16	140.68	31.67			
11.13	0.107	0.024	0.011	0.035					1.28	210.92				
12.13	0.126	0.018	0.011	0.029					1.27	285.56				
13.13	0.138	0.016	0.012	0.028					0.87	358.56	35.00			
14.13	0.144	0.012	0.011	0.023					1.16	413.08				
15.13	0.152	0.010	0.011	0.021					0.86	480.28				
16.13						0.085	0.002	0.004	0.11	525.88	32.22			
17.13									0.25	533.60				
18.13									0.13	547.64				
19.13									0.02	554.56	29.44			
20.13									0.0	555.60				
21.13									0.0	555.60				
22.13									0.0	555.60	27.22			
23.13									0.0	555.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-20-76
% POSSIBLE MINUTES SUNSHINE, 74
RDU AIRPORT MAXIMUM TEMPERATURE, 33.89 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.004	0.031	0.012	0.043	0.0				0.0	0.0				
1.30	0.003	0.032	0.012	0.044	0.0				0.0	0.0	21.11			
2.30	0.002	0.030	0.010	0.040	0.0				0.0	0.0				
3.30	0.001	0.045	0.211	0.256	0.0				0.0	0.0				
4.30	0.0	0.844	0.196	1.040	0.0				0.0	0.0	18.89			
5.30	0.0	0.800	0.210	1.010	0.002				0.03	0.54				
6.30	0.0	0.777	0.220	0.997	0.005				0.21	5.58				
7.30	0.0	0.745	0.240	0.985	0.005				0.46	22.68	21.11			
8.30	0.0	0.644	0.294	0.938	0.017				0.73	55.14		2.32	8.00	
9.30	0.0	0.420	0.350	0.770	0.045				1.00	103.80				
10.30	0.005	0.215	0.366	0.581	0.075	0.009[a]	0.322	0.479	1.03	164.34	28.33			
11.30	0.026	0.094	0.325	0.419	0.105				1.14	228.12				
12.30	0.070	0.042	0.257	0.299	0.125		0.157		1.10	295.80				
13.30	0.130	0.022	0.175	0.197	0.125				1.24	364.32	31.67			
14.30	0.185	0.016	0.108	0.124	0.120				1.15	437.10				
15.30	0.215	0.015	0.064	0.079	0.115		0.041		0.92	501.96				
16.30	0.225	0.016	0.040	0.056	0.105				0.68	552.84	30.00			
17.30	0.199	0.016	0.029	0.045	0.090	0.127	0.245	0.169	0.32	587.16				
18.30	0.160	0.014	0.023	0.037	0.075				0.18	603.84				
19.30	0.124	0.020	0.020	0.040	0.055				0.03	611.94	27.78			
20.30	0.096	0.021	0.015	0.036	0.040		0.123		0.0	613.20				
21.30	0.075	0.022	0.012	0.034	0.030				0.0	613.20				
22.30	0.058	0.027	0.012	0.039	0.020				0.0	613.20	23.89			
23.30	0.044	0.028	0.010	0.038	0.015				0.0	613.20				

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[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 95% DILUTION

DAY 2, 7-21-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.00 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	HBK1 (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.033	0.028	0.010	0.038	0.008				0.0	0.0				
1.30	0.023	0.028	0.010	0.038	0.005				0.0	0.0	22.78			
2.30	0.017	0.028	0.009	0.037	0.003		0.005		0.0	0.0				
3.30	0.010	0.028	0.009	0.037	0.0				0.0	0.0				
4.30	0.006	0.026	0.009	0.035	0.0				0.0	0.0	21.67			
5.30	0.003	0.026	0.009	0.035	0.0				0.03	0.54				
6.30	0.002	0.027	0.009	0.036	0.0				0.19	5.22				
7.30	0.009	0.027	0.010	0.037	0.0				0.42	20.76	21.67			
8.30	0.023	0.020	0.011	0.031	0.0				0.68	50.64		2.32		8.00
9.30	0.045	0.027	0.011	0.038	0.0				0.94	96.12				
10.30	0.070	0.028	0.011	0.039	0.0	0.070	0.009	0.293	1.04	154.32	30.00			
11.30	0.091	0.026	0.011	0.037	0.003				1.11	217.98				
12.30	0.107	0.021	0.011	0.032	0.003				1.24	286.92				
13.30	0.120	0.012	0.011	0.023	0.0				1.11	358.98	32.22			
14.30	0.126	0.019	0.011	0.030	0.0				0.96	422.88				
15.30	0.129	0.018	0.010	0.028	0.003				0.91	479.58				
16.30	0.135	0.017	0.010	0.027	0.003				0.65	529.50	33.33			
17.30	0.131	0.015	0.010	0.025	0.003	0.069	0.008	0.155	0.38	563.64				
18.30	0.125	0.013	0.010	0.023	0.0				0.13	581.94				
19.30	0.117	0.013	0.010	0.023	0.0				0.02	587.76	31.11			
20.30	0.110	0.013	0.009	0.022	0.0				0.0	588.60				
21.30	0.103	0.019	0.007	0.026	0.0				0.0	588.60				
22.30	0.097	0.020	0.008	0.028	0.0				0.0	588.60	25.56			
23.30	0.091	0.022	0.007	0.029	0.0				0.0	588.60				

RTI SMOG CHAMBER STUDY; USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 95% DILUTION

DAY 3, 7-22-76
% POSSIBLE MINUTES SUNSHINE, 69
RDU AIRPORT MAXIMUM TEMPERATURE, 36.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NMHC (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.085	0.025	0.008	0.033	0.0				0.0	0.0				
1.30	0.079	0.027	0.007	0.034	0.0				0.0	0.0	23.89			
2.30	0.073	0.029	0.008	0.037	0.0				0.0	0.0				
3.30	0.065	0.030	0.008	0.038	0.0				0.0	0.0				
4.30	0.057	0.032	0.008	0.040	0.0				0.0	0.0	22.78			
5.30	0.050	0.033	0.009	0.042	0.0				0.03	0.54				
6.30	0.041	0.032	0.010	0.042	0.0				0.20	5.40				
7.30	0.037	0.038	0.012	0.050	0.0				0.40	21.00	22.78			
8.30	0.049	0.038	0.012	0.050	0.0				0.68	50.04				
9.30	0.073	0.034	0.012	0.046	0.0	0.079	0.008	0.032	0.88	94.44				
10.30	0.094	0.031	0.012	0.043	0.0				1.16	152.28	31.67			
11.30	0.115	0.027	0.011	0.038	0.0				1.24	223.32				
12.30	0.133	0.021	0.010	0.031	0.0				1.27	298.26				
13.30	0.140	0.019	0.010	0.029	0.0				0.87	367.26	35.00			
14.30	0.147	0.018	0.010	0.028	0.0				1.16	424.68				
15.30	0.152	0.013	0.010	0.023	0.0				0.86	488.88				
16.30						0.072	0.008	0.087	0.11	526.98	32.22			
17.30									0.25	536.10				
18.30									0.13	548.94				
19.30									0.02	554.76	29.44			
20.30									0.0	555.60				
21.30									0.0	555.60				
22.30									0.0	555.60	27.22			
23.30									0.0	555.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, PYRROLE , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-20-76
% POSSIBLE MINUTES SUNSHINE, 74
HOU AIRPORT MAXIMUM TEMPERATURE, 33.89 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.0	0.031	0.001	0.032					0.0	0.0				
1.47	0.0	0.030	0.001	0.031					0.0	0.0	21.11			
2.47	0.0	0.030	0.001	0.031					0.0	0.0				
3.47	0.0	0.050	0.195	0.245					0.0	0.0				
4.47	0.0	0.703	0.185	0.888					0.0	0.0	18.89			
5.47	0.0	0.770	0.186	0.956					0.03	0.84				
6.47	0.0	0.680	0.271	0.951					0.21	7.68				
7.47	0.003	0.175	0.675	0.850					0.46	27.28	21.11			
8.47	0.058	0.040	0.430	0.470					0.73	62.44		2.05	8.00	
9.47	0.041	0.046	0.286	0.332					1.00	113.80				
10.47	0.042	0.036	0.200	0.236		0.067	0.181	0.505	1.03	174.64	28.33			
11.47	0.045	0.030	0.144	0.174					1.14	239.52				
12.47	0.047	0.027	0.105	0.132			0.086		1.10	306.80				
13.47	0.048	0.021	0.077	0.098					1.24	376.72	31.67			
14.47	0.050	0.017	0.057	0.074					1.15	448.60				
15.47	0.052	0.017	0.041	0.058			0.040		0.92	511.16				
16.47	0.052	0.017	0.032	0.049					0.68	559.64	30.00			
17.47	0.048	0.017	0.026	0.043		0.262	0.088	0.100	0.32	590.36				
18.47	0.040	0.019	0.023	0.042					0.18	605.64				
19.47	0.031	0.019	0.020	0.039					0.03	612.24	27.78			
20.47	0.023	0.021	0.015	0.036			0.089		0.0	613.20				
21.47	0.019	0.023	0.014	0.037					0.0	613.20				
22.47	0.013	0.027	0.012	0.039					0.0	613.20	23.89			
23.47	0.011	0.028	0.011	0.039					0.0	613.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, PYRROLE , 95% DILUTION

DAY 2, 7-21-76
1 POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.00 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.009	0.028	0.010	0.038					0.0	0.0				
1.47	0.006	0.028	0.009	0.037					0.0	0.0	22.78			
2.47	0.003	0.027	0.008	0.035			0.006		0.0	0.0				
3.47	0.002	0.027	0.008	0.035					0.0	0.0				
4.47	0.001	0.026	0.008	0.034					0.0	0.0	21.67			
5.47	0.0	0.025	0.007	0.032					0.03	0.84				
6.47	0.001	0.027	0.007	0.034					0.19	7.12				
7.47	0.008	0.027	0.008	0.035					0.42	24.96	21.67			
8.47	0.018	0.020	0.008	0.028					0.68	57.44		2.05		8.00
9.47	0.033	0.026	0.008	0.034					0.94	105.52				
10.47	0.047	0.027	0.009	0.036		0.062	0.009	0.269	1.04	164.72	30.00			
11.47	0.061	0.025	0.009	0.034					1.11	229.08				
12.47	0.073	0.022	0.009	0.031					1.24	299.32				
13.47	0.084	0.014	0.009	0.023					1.11	370.08	32.22			
14.47	0.090	0.019	0.009	0.028					0.96	432.48				
15.47	0.099	0.018	0.010	0.028					0.91	488.68				
16.47	0.101	0.017	0.009	0.026					0.65	536.00	33.33			
17.47	0.100	0.015	0.009	0.024		0.044	0.007	0.037	0.38	567.44				
18.47	0.095	0.012	0.010	0.022					0.13	583.24				
19.47	0.090	0.013	0.009	0.022					0.02	587.96	31.11			
20.47	0.084	0.013	0.008	0.021					0.0	588.60				
21.47	0.078	0.019	0.008	0.027					0.0	588.60				
22.47	0.074	0.020	0.008	0.028					0.0	588.60	25.56			
23.47	0.070	0.022	0.007	0.029					0.0	588.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3,   PYRROLE   , 95% DILUTION   PAGE 3

DAY 3, 7-22-76
% POSSIBLE MINUTES SUNSHINE, 69
RDU AIRPORT MAXIMUM TEMPERATURE, 36.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.065	0.024	0.007	0.031					0.0	0.0				
1.47	0.061	0.026	0.006	0.032					0.0	0.0	23.89			
2.47	0.056	0.029	0.006	0.035					0.0	0.0				
3.47	0.052	0.030	0.006	0.036					0.0	0.0				
4.47	0.046	0.032	0.007	0.039					0.0	0.0	22.78			
5.47	0.041	0.031	0.008	0.039					0.03	0.84				
6.47	0.035	0.032	0.008	0.040					0.20	7.40				
7.47	0.033	0.038	0.010	0.048					0.40	25.00	22.78			
8.47	0.045	0.038	0.011	0.049					0.68	56.84				
9.47	0.072	0.034	0.012	0.046		0.099	0.009	0.002	0.88	103.24				
10.47	0.095	0.031	0.012	0.043					1.16	163.88	31.67			
11.47	0.115	0.028	0.010	0.038					1.24	235.72				
12.47	0.131	0.022	0.010	0.032					1.27	310.96				
13.47	0.140	0.020	0.010	0.030					0.87	375.96	35.00			
14.47	0.144	0.018	0.010	0.028					1.16	436.28				
15.47	0.147	0.013	0.010	0.023					0.86	497.48				
16.47						0.065	0.013	0.008	0.11	528.08	32.22			
17.47									0.25	538.60				
18.47									0.13	550.24				
19.47									0.02	554.96	29.44			
20.47									0.0	555.60				
21.47									0.0	555.60				
22.47									0.0	555.60				
23.47									0.0	555.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-20-76
% POSSIBLE MINUTES SUNSHINE, 74
RDU AIRPORT MAXIMUM TEMPERATURE, 33.89 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.0	0.034	0.004	0.038					0.0	0.0				
1.63	0.0	0.031	0.003	0.034					0.0	0.0	21.11			
2.63	0.0	0.030	0.003	0.033					0.0	0.0				
3.63	0.0	0.048	0.193	0.241					0.0	0.0				
4.63	0.0	0.268	0.188	0.456					0.0	0.0	18.89			
5.63	0.0	0.810	0.195	1.005					0.03	1.14				
6.63	0.0	0.765	0.237	1.002					0.21	9.78				
7.63	0.0	0.570	0.407	0.977					0.46	31.88	21.11			
8.63	0.020	0.110	0.725	0.835					0.73	69.74		2.30	8.00	
9.63	0.745	0.019	0.510	0.529					1.00	123.80				
10.63	0.935	0.013	0.335	0.348		1.309	0.059	1.096	1.03	184.94	28.33			
11.63	0.893	0.012	0.262	0.274					1.14	250.92				
12.63	0.859	0.010	0.203	0.213			0.027		1.10	317.80				
13.63	0.805	0.008	0.157	0.165					1.24	389.12	31.67			
14.63	0.746	0.008	0.119	0.127					1.15	460.10				
15.63	0.669	0.010	0.089	0.099			0.020		0.92	520.36				
16.63	0.580	0.010	0.066	0.076					0.68	566.44	30.00			
17.63	0.488	0.012	0.049	0.061		1.108	0.054	0.740	0.32	593.56				
18.63	0.403	0.013	0.039	0.052					0.18	607.44				
19.63	0.333	0.016	0.029	0.045					0.03	612.54	27.78			
20.63	0.278	0.019	0.022	0.041			0.015		0.0	613.20				
21.63	0.233	0.020	0.020	0.040					0.0	613.20				
22.63	0.197	0.021	0.017	0.038					0.0	613.20	23.89			
23.63	0.167	0.021	0.014	0.035					0.0	613.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 95% DILUTION

PAGE 2

DAY 2, 7-21-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.00 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.140	0.022	0.012	0.034					0.0	0.0				
1.63	0.119	0.022	0.011	0.033					0.0	0.0	22.78			
2.63	0.101	0.022	0.010	0.032			0.003		0.0	0.0				
3.63	0.085	0.021	0.009	0.030					0.0	0.0				
4.63	0.071	0.021	0.008	0.029					0.0	0.0	21.67			
5.63	0.060	0.021	0.008	0.029					0.03	1.14				
6.63	0.050	0.021	0.008	0.029					0.19	9.02				
7.63	0.043	0.021	0.007	0.028					0.42	29.16	21.67			
8.63	0.044	0.016	0.007	0.023					0.68	64.24		2.30		8.00
9.63	0.055	0.020	0.008	0.028					0.94	114.92				
10.63	0.070	0.020	0.009	0.029		0.108	0.011	0.386	1.04	175.12	30.00			
11.63	0.083	0.020	0.009	0.029					1.11	240.18				
12.63	0.093	0.018	0.009	0.027					1.24	311.72				
13.63	0.103	0.010	0.010	0.020					1.11	381.18	32.22			
14.63	0.106	0.012	0.010	0.022					0.96	442.08				
15.63	0.111	0.011	0.009	0.020					0.91	497.78				
16.63	0.111	0.011	0.010	0.021					0.65	542.50	33.33			
17.63	0.107	0.009	0.009	0.018		0.107	0.011	0.334	0.38	571.24				
18.63	0.103	0.009	0.009	0.018					0.13	584.54				
19.63	0.098	0.009	0.008	0.017					0.02	588.16	31.11			
20.63	0.095	0.010	0.008	0.018					0.0	588.60				
21.63	0.092	0.013	0.007	0.020					0.0	588.60				
22.63	0.089	0.016	0.007	0.023					0.0	588.60	25.56			
23.63	0.086	0.020	0.006	0.026					0.0	588.60				

RTI SMOG CHAMBER STUDY; USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 95% DILUTION

DAY 3, 7-22-76
% POSSIBLE MINUTES SUNSHINE, 69
RDU AIRPORT MAXIMUM TEMPERATURE, 36.67 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.084	0.020	0.007	0.027					0.0	0.0				
1.63	0.082	0.022	0.005	0.027					0.0	0.0	23.89			
2.63	0.080	0.025	0.005	0.030					0.0	0.0				
3.63	0.078	0.026	0.004	0.030					0.0	0.0				
4.63	0.076	0.028	0.005	0.033					0.0	0.0	22.78			
5.63	0.074	0.029	0.006	0.035					0.03	1.14				
6.63	0.072	0.030	0.007	0.037					0.20	9.40				
7.63	0.068	0.032	0.008	0.040					0.40	29.00	22.78			
8.63	0.069	0.032	0.008	0.040					0.68	63.64				
9.63	0.077	0.030	0.009	0.039		0.108	0.008	0.012	0.88	112.04				
10.63	0.093	0.028	0.010	0.038					1.16	175.48	31.67			
11.63	0.108	0.023	0.010	0.033					1.24	248.12				
12.63	0.123	0.020	0.010	0.030					1.27	323.66				
13.63	0.144	0.017	0.010	0.027					0.87	384.66	35.00			
14.63	0.135	0.014	0.010	0.024					1.16	447.88				
15.63	0.137	0.010	0.010	0.020					0.86	506.08				
16.63						0.096	0.008	0.038	0.11	529.18	32.22			
17.63									0.25	541.10				
18.63									0.13	551.54				
19.63									0.02	555.16	29.44			
20.63									0.0	555.60				
21.63									0.0	555.60				
22.63								-	0.0	555.60	27.22			
23.63									0.0	555.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

PAGE 1

DAY 1, 7-28-76
% POSSIBLE MINUTES SUNSHINE, 45
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.0	0.006	0.004	0.010	0.0				0.0	0.0				
1.13	0.0	0.009	0.002	0.011	0.0				0.0	0.0	23.89			
2.13	0.0	0.009	0.002	0.011	0.0				0.0	0.0				
3.13	0.0	0.009	0.116	0.125	0.0				0.0	0.0				
4.13	0.0	0.161	0.225	0.386	0.0				0.0	0.0	22.78			
5.13	0.0	0.798	0.210	1.008	0.004				0.01	0.08				
6.13	0.0	0.763	0.217	0.980	0.010				0.17	1.96				
7.13	0.0	0.660	0.297	0.957	0.077				0.39	13.92	23.89			
8.13	0.0	0.430	0.484	0.914	0.400				0.61	39.08				
9.13	0.410	0.026	0.531	0.557	1.540				0.53	75.04				
10.13	0.745	0.008	0.077	0.085	1.610	0.039[b]	0.029	0.889	1.11	111.48	31.11			
11.13	0.693	0.022	0.048	0.070	1.540				1.19	178.72				
12.13	0.643	0.011	0.047	0.058	1.456				1.18	250.04				
13.13	0.580	0.023	0.045	0.068	1.358				0.88	318.44	32.78			
14.13	0.515	0.016	0.052	0.068	1.260				1.01	372.28				
15.13	0.478	0.022	0.045	0.067	1.220				0.84	431.52				
16.13	0.434	0.012	0.058	0.070	1.150	0.043[b]	0.035	0.856	0.55	479.60	32.22			
17.13	0.406	0.026	0.045	0.071	1.090				0.31	510.68				
18.13	0.382	0.028	0.040	0.068	1.040				0.10	527.60				
19.13	0.356	0.037	0.037	0.074	0.980				0.01	532.88	27.78			
20.13	0.335	0.043	0.035	0.078	0.920				0.0	533.40				
21.13	0.304	0.055	0.035	0.090	0.770				0.0	533.40				
22.13	0.273	0.068	0.036	0.104	0.660				0.0	533.40	23.89			
23.13	0.241	0.074	0.036	0.110	0.520				0.0	533.40				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

[b] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 0% DILUTION

DAY 2, 7-29-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.56 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.207	0.076	0.040	0.116	0.360				0.0	0.0				
1.13	0.178	0.076	0.043	0.119	0.210				0.0	0.0	23.89			
2.13	0.153	0.077	0.044	0.121	0.112				0.0	0.0				
3.13	0.128	0.073	0.045	0.118	0.040				0.0	0.0				
4.13	0.106	0.066	0.046	0.112	0.0				0.0	0.0	22.78			
5.13	0.089	0.064	0.047	0.111	0.0				0.02	0.16				
6.13	0.073	0.062	0.048	0.110	0.0				0.17	2.56				
7.13	0.068	0.069	0.049	0.118	0.0				0.39	14.52	23.89			
8.13	0.097	0.077	0.052	0.129	0.0				0.68	40.24				
9.13	0.159	0.095	0.053	0.148	0.040				0.90	82.80				
10.13	0.213	0.096	0.045	0.141	0.056	0.177[b]	0.022	0.063	1.10	138.40	30.00			
11.13	0.260	0.094	0.043	0.137	0.056				0.96	203.28				
12.13	0.276	0.074	0.040	0.114	0.042				1.28	263.44				
13.13	0.288	0.063	0.036	0.099	0.042				1.13	339.04	32.22			
14.13	0.297	0.057	0.037	0.094	0.028				0.68	403.24				
15.13	0.285	0.038	0.038	0.076	0.028				0.60	443.40				
16.13	0.277	0.044	0.035	0.079	0.028	0.153[b]	0.018	0.321	0.31	477.08	34.44			
17.13	0.263	0.035	0.032	0.067	0.0				0.17	494.56				
18.13	0.250	0.036	0.028	0.064	0.0				0.07	503.96				
19.13	0.230	0.045	0.029	0.074	0.0				0.01	507.68	31.67			
20.13	0.206	0.038	0.030	0.068	0.0				0.0	508.20				
21.13	0.180	0.043	0.032	0.075	0.0				0.0	508.20				
22.13	0.157	0.040	0.034	0.074	0.0				0.0	508.20	26.11			
23.13	0.140	0.033	0.036	0.069	0.0				0.0	508.20				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

[b] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 0% DILUTION

DAY 3, 7-30-76
% POSSIBLE MINUTES SUNSHINE, 65
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NOKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.126	0.026	0.037	0.063	0.0				0.0	0.0				
1.13	0.113	0.024	0.041	0.065	0.0				0.0	0.0	25.00			
2.13	0.101	0.024	0.042	0.066	0.0				0.0	0.0				
3.13	0.092	0.023	0.044	0.067	0.0				0.0	0.0				
4.13	0.083	0.023	0.046	0.069	0.0				0.0	0.0	23.33			
5.13	0.074	0.023	0.053	0.076	0.0				0.02	0.16				
6.13	0.065	0.023	0.075	0.098	0.0				0.15	2.40				
7.13	0.069	0.027	0.076	0.103	0.0				0.38	13.24	25.00			
8.13	0.103	0.032	0.065	0.097	0.0				0.69	38.52				
9.13	0.151	0.038	0.055	0.093	0.0				0.94	81.92				
10.13	0.196	0.045	0.045	0.090	0.0	0.205	0.040	0.041	1.15	140.00	31.11			
11.13	0.238	0.036	0.041	0.077	0.0				1.18	209.24				
12.13	0.273	0.045	0.035	0.080	0.0				1.32	281.16				
13.13	0.289	0.059	0.033	0.092	0.0				1.21	359.48	33.33			
14.13	0.292	0.035	0.031	0.066	0.0				1.13	431.44				
15.13	0.290	0.035	0.037	0.072	0.0	0.348	0.014	0.011	0.89	497.32				
16.13	0.283	0.023	0.029	0.052	0.0				0.61	548.48	34.44			
17.13	0.271								0.10	581.00				
18.13									0.02	586.36				
19.13									0.0	587.40	25.00			
20.13									0.0	587.40				
21.13									0.0	587.40				
22.13									0.0	587.40	23.33			
23.13									0.0	587.40				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2,METHYL DISULFIDE, 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

PAGE 1

DAY 1, 7-28-76
% POSSIBLE MINUTES SUNSHINE, 45
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.011	0.006	0.004	0.010	0.0				0.0	0.0				
1.30	0.010	0.008	0.004	0.012	0.0				0.0	0.0	23.89			
2.30	0.008	0.008	0.003	0.011	0.0				0.0	0.0				
3.30	0.006	0.008	0.230	0.238	0.0				0.0	0.0				
4.30	0.0	0.161	0.223	0.384	0.0				0.0	0.0	22.78			
5.30	0.0	0.797	0.239	1.036	0.008				0.01	0.18				
6.30	0.0	0.640	0.366	1.006	0.210				0.17	3.66				
7.30	0.0	0.349	0.589	0.938	1.610				0.39	17.82	23.89			
8.30	0.605	0.010	0.194	0.204					0.61	45.18				
9.30	0.661	0.021	0.045	0.066	1.890				0.53	80.34				
10.30	0.651	0.017	0.032	0.049	1.820	0.017[b]	0.015	0.728	1.11	122.58	31.11			
11.30	0.615	0.022	0.030	0.052	1.790				1.19	190.62				
12.30	0.596	0.019	0.031	0.050	1.720				1.18	261.84				
13.30	0.566	0.023	0.029	0.052	1.680				0.88	327.24	32.78			
14.30	0.530	0.023	0.031	0.054	1.610				1.01	382.38				
15.30	0.506	0.017	0.041	0.058	1.580				0.84	439.92				
16.30	0.476	0.017	0.032	0.049	1.510	0.014[b]	0.016	0.671	0.55	485.10	32.22			
17.30	0.455	0.028	0.028	0.056	1.480				0.31	513.78				
18.30	0.435	0.033	0.024	0.057	1.460				0.10	528.60				
19.30	0.414	0.038	0.022	0.060	1.400				0.01	532.98	27.78			
20.30	0.392	0.050	0.022	0.072	1.320				0.0	533.40				
21.30	0.355	0.062	0.025	0.087	1.090				0.0	533.40				
22.30	0.314	0.068	0.026	0.094	0.850				0.0	533.40	23.89			
23.30	0.270	0.070	0.028	0.098	0.520				0.0	533.40				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

[b] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2,METHYL DISULFIDE, 0% DILUTION

DAY 2, 7-29-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.56 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.227	0.074	0.029	0.103	0.240				0.0	0.0				
1.30	0.193	0.079	0.029	0.108	0.080				0.0	0.0	23.89			
2.30	0.165	0.077	0.031	0.108	0.003				0.0	0.0				
3.30	0.140	0.071	0.031	0.102	0.0				0.0	0.0				
4.30	0.122	0.064	0.033	0.097	0.0				0.0	0.0	22.78			
5.30	0.105	0.061	0.034	0.095	0.0				0.02	0.36				
6.30	0.088	0.061	0.037	0.098	0.0				0.17	4.26				
7.30	0.084	0.070	0.039	0.109	0.0				0.39	18.42	23.89			
8.30	0.109	0.081	0.041	0.122	0.0				0.68	47.04				
9.30	0.155	0.109	0.041	0.150	0.0				0.90	91.80				
10.30	0.206	0.111	0.039	0.150	0.0	0.194	0.018	0.048	1.10	149.40	30.00			
11.30	0.257	0.106	0.035	0.141	0.0				0.96	212.88				
12.30	0.282	0.107	0.035	0.142	0.0				1.28	276.24				
13.30	0.304	0.077	0.031	0.108	0.0				1.13	350.34	32.22			
14.30	0.313	0.071	0.029	0.100	0.0				0.68	410.04				
15.30	0.301	0.069	0.030	0.099	0.0				0.60	449.40				
16.30	0.293	0.043	0.027	0.070	0.0	0.199	0.018	0.034	0.31	480.18	34.44			
17.30	0.276	0.053	0.028	0.081	0.0				0.17	496.26				
18.30	0.264	0.042	0.026	0.068	0.0				0.07	504.66				
19.30	0.224	0.041	0.026	0.067	0.0				0.01	507.78	31.67			
20.30	0.205	0.046	0.029	0.075	0.0				0.0	508.20				
21.30	0.187	0.039	0.031	0.070	0.0				0.0	508.20				
22.30	0.171	0.040	0.033	0.073	0.0				0.0	508.20	26.11			
23.30	0.157	0.040	0.036	0.076	0.0				0.0	508.20				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2,METHYL DISULFIDE, 0% DILUTION

DAY 3, 7-30-76
% POSSIBLE MINUTES SUNSHINE, 65
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (LST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.145	0.030	0.038	0.068	0.0				0.0	0.0				
1.30	0.134	0.024	0.039	0.063	0.0				0.0	0.0	25.00			
2.30	0.123	0.022	0.041	0.063	0.0				0.0	0.0				
3.30	0.113	0.022	0.047	0.069	0.0				0.0	0.0				
4.30	0.104	0.022	0.047	0.069	0.0				0.0	0.0	23.33			
5.30	0.094	0.020	0.049	0.069	0.0				0.02	0.36				
6.30	0.085	0.021	0.056	0.077	0.0				0.15	3.90				
7.30	0.091	0.022	0.071	0.093	0.0				0.38	17.04	25.00			
8.30	0.113	0.031	0.066	0.097	0.0				0.69	45.42				
9.30	0.151	0.038	0.059	0.097	0.0				0.94	91.32				
10.30	0.203	0.041	0.050	0.091	0.0	0.207	0.039	0.071	1.15	151.50	31.11			
11.30	0.256	0.050	0.040	0.090	0.0				1.18	221.04				
12.30	0.297	0.041	0.032	0.073	0.0				1.32	294.36				
13.30	0.315	0.047	0.030	0.077	0.0				1.21	371.58	33.33			
14.30	0.323	0.069	0.027	0.096	0.0				1.13	442.74				
15.30	0.324	0.043	0.026	0.069	0.0	0.379	0.014	0.084	0.89	506.22				
16.30	0.320	0.032	0.025	0.057	0.0				0.61	554.58	34.44			
17.30									0.10	582.00				
18.30									0.02	586.56				
19.30									0.0	587.40	25.00			
20.30									0.0	587.40				
21.30									0.0	587.40				
22.30									0.0	587.40	23.33			
23.30									0.0	587.40				

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[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-28-76
% POSSIBLE MINUTES SUNSHINE, 45
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.0	0.006	0.004	0.010	0.0				0.0	0.0				
1.47	0.0	0.007	0.004	0.011	0.0				0.0	0.0	23.89			
2.47	0.0	0.008	0.004	0.012	0.0				0.0	0.0				
3.47	0.0	0.008	0.241	0.249	0.0				0.0	0.0				
4.47	0.0	0.154	0.220	0.374	0.0				0.0	0.0	22.78			
5.47	0.0	0.773	0.235	1.008	0.006				0.01	0.28				
6.47	0.0	0.603	0.372	0.975	0.020				0.17	5.36				
7.47	0.295	0.006	0.530	0.536	0.250				0.39	21.72	23.89			
8.47	0.448	0.001	0.070	0.071	0.480				0.61	51.28				
9.47	0.395	0.001	0.035	0.036	0.490				0.53	85.64				
10.47	0.336	0.0	0.029	0.029	0.490	0.076[b]	0.005	0.812	1.11	133.68	31.11			
11.47	0.275	0.0	0.026	0.026	0.460				1.19	202.52				
12.47	0.235	0.001	0.030	0.031	0.430				1.18	273.64				
13.47	0.207	0.002	0.027	0.029	0.420				0.88	336.04	32.78			
14.47	0.178	0.003	0.033	0.036	0.380				1.01	392.48				
15.47	0.164	0.005	0.030	0.035	0.350				0.84	448.32				
16.47	0.143	0.004	0.038	0.042	0.340	0.083[b]	0.009	0.795	0.55	490.60	32.22			
17.47	0.130	0.007	0.031	0.038	0.320				0.31	516.88				
18.47	0.116	0.009	0.026	0.035	0.280				0.10	529.60				
19.47	0.105	0.015	0.024	0.039	0.250				0.01	533.08	27.78			
20.47	0.094	0.022	0.022	0.044	0.210				0.0	533.40				
21.47	0.081	0.038	0.022	0.060	0.130				0.0	533.40				
22.47	0.066	0.055	0.021	0.076	0.080				0.0	533.40	23.89			
23.47	0.052	0.065	0.021	0.086	0.040				0.0	533.40				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

[b] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 0% DILUTION

DAY 2, 7-29-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.56 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.040	0.073	0.020	0.093	0.010				0.0	0.0				
1.47	0.031	0.075	0.020	0.095	0.0				0.0	0.0	23.89			
2.47	0.024	0.076	0.022	0.098	0.0				0.0	0.0				
3.47	0.018	0.068	0.023	0.091	0.0				0.0	0.0				
4.47	0.014	0.063	0.023	0.086	0.0				0.0	0.0	22.78			
5.47	0.011	0.061	0.024	0.085	0.0				0.02	0.56				
6.47	0.010	0.063	0.026	0.089	0.0				0.17	5.96				
7.47	0.032	0.068	0.034	0.102	0.0				0.39	22.32	23.89			
8.47	0.095	0.086	0.036	0.122	0.0				0.68	53.84				
9.47	0.152	0.107	0.032	0.139	0.0				0.90	100.80				
10.47	0.185	0.107	0.028	0.135	0.0	0.047[b]	0.008	0.010	1.10	160.40	30.00			
11.47	0.201	0.104	0.022	0.126	0.0				0.96	222.48				
12.47	0.185	0.101	0.022	0.123	0.0				1.28	289.04				
13.47	0.194	0.080	0.022	0.102	0.0				1.13	361.64	32.22			
14.47	0.183	0.075	0.018	0.093	0.0				0.68	416.84				
15.47	0.162	0.073	0.018	0.091	0.0				0.60	455.40				
16.47	0.158	0.046	0.017	0.063	0.0	0.036[b]	0.009	0.075	0.31	483.28	34.44			
17.47	0.141	0.052	0.015	0.067	0.0				0.17	497.96				
18.47	0.128	0.046	0.016	0.062	0.0				0.07	505.36				
19.47	0.105	0.046	0.016	0.062	0.0				0.01	507.88	31.67			
20.47	0.088	0.045	0.017	0.062	0.0				0.0	508.20				
21.47	0.075	0.040	0.017	0.057	0.0				0.0	508.20				
22.47	0.065	0.042	0.019	0.061	0.0				0.0	508.20	26.11			
23.47	0.057	0.040	0.021	0.061	0.0				0.0	508.20				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

[b] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY; USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 0% DILUTION

DAY 3, 7-30-76
% POSSIBLE MINUTES SUNSHINE, 65
RDU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO[a] (PPM)	NO2 (PPM)	NOX[a] (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.049	0.030	0.023	0.053	0.0				0.0	0.0				
1.47	0.043	0.023	0.025	0.048	0.0				0.0	0.0	25.00			
2.47	0.038	0.023	0.029	0.052	0.0				0.0	0.0				
3.47	0.028	0.022	0.032	0.054	0.0				0.0	0.0				
4.47	0.024	0.022	0.036	0.058	0.0				0.0	0.0	23.33			
5.47	0.023	0.020	0.040	0.060	0.0				0.02	0.56				
6.47	0.052	0.020	0.047	0.067	0.0				0.15	5.40				
7.47	0.093	0.023	0.050	0.073	0.0				0.38	20.84	25.00			
8.47	0.146	0.033	0.044	0.077	0.0				0.69	52.32				
9.47	0.207	0.037	0.036	0.073	0.0				0.94	100.72				
10.47	0.251	0.045	0.032	0.077	0.0	0.060	0.008	0.077	1.15	163.00	31.11			
11.47	0.277	0.053	0.027	0.080	0.0				1.18	232.84				
12.47	0.280	0.046	0.025	0.071	0.0				1.32	307.56				
13.47	0.280	0.047	0.023	0.070	0.0				1.21	383.68	33.33			
14.47	0.274	0.060	0.021	0.081	0.0	0.314	0.011	0.040	1.13	454.04				
15.47	0.270	0.044	0.019	0.063	0.0				0.89	515.12				
16.47	0.264	0.033	0.018	0.051	0.0				0.61	560.68	34.44			
17.47									0.10	583.00				
18.47									0.02	586.76				
19.47									0.0	587.40	25.00			
20.47									0.0	587.40				
21.47									0.0	587.40				
22.47									0.0	587.40	23.33			
23.47									0.0	587.40				

[a] The NO and NO_x readings in this run may be artificially high following the afternoon of 28 July 1976 due to either zero drift in the instrument or some unexplained interferent or sampling artifact.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 7-28-76
% POSSIBLE MINUTES SUNSHINE, 45
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.003	0.008	0.004	0.012					0.0	0.0				
1.63	0.002	0.009	0.004	0.013					0.0	0.0	23.89			
2.63	0.001	0.008	0.003	0.011					0.0	0.0				
3.63	0.0	0.008	0.233	0.241					0.0	0.0				
4.63	0.0	0.074	0.225	0.299					0.0	0.0	22.78			
5.63	0.0	0.820	0.239	1.059					0.01	0.38				
6.63	0.0	0.745	0.305	1.050					0.17	7.06				
7.63	0.0	0.506	0.506	1.012					0.39	25.62	23.89			
8.63	0.095	0.054	0.885	0.939					0.61	57.38				
9.63	0.925	0.044	0.576	0.620					0.53	90.94				
10.63	1.100	0.041	0.456	0.497		1.402	0.093	1.399	1.11	144.78	31.11			
11.63	1.212	0.026	0.387	0.413					1.19	214.42				
12.63	1.280	0.018	0.322	0.340					1.18	285.44				
13.63	1.266	0.014	0.263	0.277					0.88	344.84	32.78			
14.63	1.200	0.013	0.220	0.233					1.01	402.58				
15.63	1.150	0.013	0.181	0.194					0.84	456.72				
16.63	1.131	0.013	0.158	0.171		0.397	0.101	1.020	0.55	496.10	32.22			
17.63	1.082	0.015	0.134	0.149					0.31	519.98				
18.63	0.950	0.016	0.114	0.130					0.10	530.60				
19.63	0.906	0.022	0.101	0.123					0.01	533.18	27.78			
20.63	0.861	0.016	0.084	0.100					0.0	533.40				
21.63	0.815	0.030	0.077	0.107					0.0	533.40				
22.63	0.782	0.038	0.068	0.106					0.0	533.40	23.89			
23.63	0.755	0.041	0.065	0.106					0.0	533.40				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION

DAY 2, 7-29-76
% POSSIBLE MINUTES SUNSHINE, 70
RDU AIRPORT MAXIMUM TEMPERATURE, 35.56 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.723	0.044	0.059	0.103					0.0	0.0				
1.63	0.690	0.051	0.056	0.107					0.0	0.0	23.89			
2.63	0.665	0.048	0.053	0.101					0.0	0.0				
3.63	0.636	0.047	0.050	0.097					0.0	0.0				
4.63	0.613	0.046	0.049	0.095					0.0	0.0	22.78			
5.63	0.586	0.046	0.050	0.096					0.02	0.76				
6.63	0.549	0.047	0.058	0.105					0.17	7.66				
7.63	0.500	0.058	0.074	0.132					0.39	26.22	23.89			
8.63	0.443	0.101	0.078	0.179					0.68	60.64				
9.63	0.430	0.101	0.078	0.179					0.90	109.80				
10.63	0.458	0.095	0.075	0.170		0.554	0.020	0.269	1.10	171.40	30.00			
11.63	0.500	0.100	0.068	0.168					0.96	232.08				
12.63	0.501	0.083	0.059	0.142					1.28	301.84				
13.63	0.538	0.076	0.055	0.131					1.13	372.94	32.22			
14.63	0.525	0.068	0.043	0.111					0.68	423.64				
15.63	0.487	0.057	0.042	0.099					0.60	461.40				
16.63	0.480	0.042	0.037	0.079		0.490	0.016	0.277	0.31	486.38	34.44			
17.63	0.458	0.044	0.034	0.078					0.17	499.66				
18.63	0.427	0.045	0.029	0.074					0.07	506.06				
19.63	0.418	0.044	0.029	0.073					0.01	507.98	31.67			
20.63	0.402	0.040	0.024	0.064					0.0	508.20				
21.63	0.387	0.038	0.023	0.061					0.0	508.20				
22.63	0.372	0.041	0.022	0.063					0.0	508.20	26.11			
23.63	0.357	0.038	0.021	0.059					0.0	508.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION

DAY 3, 7-30-76
% POSSIBLE MINUTES SUNSHINE, 65
HOU AIRPORT MAXIMUM TEMPERATURE, 37.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.346	0.028	0.020	0.048					0.0	0.0				
1.63	0.334	0.023	0.019	0.042					0.0	0.0	25.00			
2.63	0.322	0.024	0.019	0.043					0.0	0.0				
3.63	0.310	0.023	0.018	0.041					0.0	0.0				
4.63	0.297	0.023	0.020	0.043					0.0	0.0	23.33			
5.63	0.285	0.020	0.020	0.040					0.02	0.76				
6.63	0.269	0.021	0.024	0.045					0.15	6.90				
7.63	0.249	0.025	0.030	0.055					0.38	24.64	25.00			
8.63	0.226	0.033	0.033	0.066					0.69	59.22				
9.63	0.236	0.039	0.032	0.071					0.94	110.12				
10.63	0.260	0.047	0.031	0.078		0.295	0.016	0.111	1.15	174.50	31.11			
11.63	0.287	0.047	0.031	0.078					1.18	244.64				
12.63	0.311	0.054	0.028	0.082					1.32	320.76				
13.63	0.316	0.053	0.029	0.082					1.21	395.78	33.33			
14.63	0.317	0.653	0.028	0.081		0.367	0.015	0.122	1.13	465.34				
15.63	0.312	0.042	0.026	0.068					0.89	524.02				
16.63	0.306	0.032	0.027	0.059					0.61	566.78	34.44			
17.63									0.10	584.00				
18.63									0.02	586.96				
19.63									0.0	587.40	25.00			
20.63									0.0	587.40				
21.63									0.0	587.40				
22.63									0.0	587.40	23.33			
23.63									0.0	587.40				

RTI SMOG CHAMBER STUDY; USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 8-10-76
% POSSIBLE MINUTES SUNSHINE, 85
RDU AIRPORT MAXIMUM TEMPERATURE, 31.11 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.0				0.0				0.0	0.0				
1.13	0.0	0.002	0.003	0.005	0.0				0.0	0.0	21.67			
2.13	0.0	0.004	0.005	0.009	0.0				0.0	0.0				
3.13	0.0	0.764	0.0	0.764	0.0				0.0	0.0				
4.13	0.0	0.752	0.246	0.998	0.010				0.0	0.0	20.00			
5.13	0.0	0.750	0.236	0.986	0.009				0.01	0.08				
6.13	0.0	0.732	0.237	0.969	0.011				0.04	0.92				
7.13	0.0	0.677	0.280	0.957	0.039				0.11	3.88	20.00			
8.13	0.0	0.468	0.417	0.885	0.237				0.23	11.44		1.95	8.00	
9.13	0.157	0.011	0.567	0.578	0.904				0.41	26.68				
10.13	0.713	0.001	0.081	0.082	1.021	0.005[a]	0.154	0.492	0.69	53.52	25.56			
11.13	0.608	0.001	0.036	0.037	0.870				1.10	98.20				
12.13	0.494	0.001	0.029	0.030	0.736				1.03	163.64				
13.13	0.411	0.001	0.026	0.027	0.627				0.84	223.92	30.00			
14.13	0.354	0.003	0.023	0.026	0.523				0.73	273.44				
15.13	0.295	0.003	0.022	0.025	0.438				0.59	316.12				
16.13	0.251	0.003	0.021	0.024	0.370	0.011[a]	0.218	0.482	0.61	351.68	30.56			
17.13	0.213	0.003	0.019	0.022	0.320				0.28	385.64				
18.13	0.180	0.002	0.017	0.019	0.269				0.07	400.76				
19.13	0.148	0.002	0.015	0.017	0.209				0.02	404.56	27.22			
20.13	0.111	0.003	0.014	0.017	0.132				0.0	405.60				
21.13	0.081	0.002	0.014	0.016	0.075				0.0	405.60				
22.13	0.059	0.0	0.014	0.014	0.036				0.0	405.60	22.22			
23.13	0.044	0.0	0.014	0.014	0.015				0.0	405.60				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 95% DILUTION

DAY 2, 8-11-76
% POSSIBLE MINUTES SUNSHINE, 88
RDU AIRPORT MAXIMUM TEMPERATURE, 32.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.029	0.009	0.013	0.022	0.011				0.0	0.0				
1.13	0.024	0.006	0.013	0.019	0.006				0.0	0.0	18.89			
2.13	0.016	0.007	0.013	0.020	0.006				0.0	0.0				
3.13	0.011	0.008	0.013	0.021	0.0				0.0	0.0				
4.13	0.008	0.008	0.012	0.020	0.0				0.0	0.0	17.22			
5.13	0.005	0.008	0.012	0.020	0.0				0.01	0.08				
6.13	0.004	0.006	0.012	0.018	0.0				0.12	1.56				
7.13	0.010	0.010	0.013	0.023	0.0				0.36	10.68	19.44			
8.13	0.026								0.68	34.84		1.95		8.00
9.13	0.054	0.013	0.018	0.031					0.93	77.64				
10.13	0.080	0.006	0.021	0.027	0.019	0.042[a]	0.018	0.609	1.12	134.96	27.78			
11.13	0.103				0.019				1.25	203.20				
12.13	0.123				0.022				1.28	278.44				
13.13	0.142	0.019	0.026	0.045	0.024				1.24	354.92	30.00			
14.13	0.156	0.016	0.034	0.050	0.027				0.87	426.36				
15.13	0.163	0.016	0.041	0.057	0.024				0.83	478.24				
16.13	0.168	0.016	0.030	0.046	0.022	0.043[a]	0.026	0.495	0.62	526.36	31.11			
17.13	0.164	0.014	0.026	0.040	0.024				0.32	561.16				
18.13	0.157	0.014	0.023	0.037	0.022				0.10	578.60				
19.13	0.147	0.014	0.020	0.034	0.019				0.0	583.80	25.00			
20.13	0.133	0.013	0.018	0.031	0.014				0.0	583.80				
21.13	0.116	0.011	0.018	0.029	0.007				0.0	583.80				
22.13	0.102	0.010	0.017	0.027	0.006				0.0	583.80	21.67			
23.13	0.093	0.008	0.017	0.025	0.0				0.0	583.80				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 95% DILUTION

DAY 5, 8-12-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.083	0.008	0.016	0.024	0.0				0.0	0.0				
1.13	0.074	0.007	0.016	0.023	0.0				0.0	0.0	20.56			
2.13	0.066	0.007	0.015	0.022	0.0				0.0	0.0				
3.13	0.060	0.007	0.016	0.023	0.0				0.0	0.0				
4.13	0.054	0.006	0.015	0.021	0.0				0.0	0.0	19.44			
5.13	0.048	0.006	0.015	0.021	0.0				0.02	0.16				
6.13	0.043	0.006	0.016	0.022	0.0				0.17	2.56				
7.13	0.043	0.010	0.020	0.030	0.0				0.44	14.92	21.67			
8.13	0.060	0.013	0.024	0.037	0.0				0.72	43.56				
9.13	0.094	0.014	0.024	0.038	0.0				0.98	88.84				
10.13	0.130	0.014	0.022	0.036	0.007	0.132	0.019	0.483	1.11	148.68	30.00			
11.13	0.156	0.014	0.019	0.033	0.007				1.25	216.40				
12.13	0.164	0.013	0.018	0.031	0.008				1.36	292.28				
13.13	0.184	0.013	0.018	0.031	0.009				1.23	372.84	32.22			
14.13	0.199	0.012	0.016	0.028	0.010				1.10	445.60				
15.13	0.200	0.012	0.017	0.029	0.012				0.87	509.76				
16.13	0.192	0.012	0.016	0.028	0.008				0.54	559.32	31.11			
17.13	0.186	0.012	0.016	0.028	0.007	0.224	0.027	0.379	0.29	589.72				
18.13	0.178	0.012	0.014	0.026	0.007				0.03	605.04				
19.13	0.170	0.013	0.013	0.026	0.007				0.01	606.68	27.78			
20.13	0.165	0.014	0.012	0.026	0.006				0.0	607.20				
21.13	0.155	0.015	0.010	0.025	0.005				0.0	607.20				
22.13	0.148	0.017	0.010	0.027	0.004				0.0	607.20	25.00			
23.13	0.139	0.018	0.010	0.028	0.0				0.0	607.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, METHANETHIOL , 95% DILUTION

DAY 4, 8-13-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	HBK1 (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.131	0.020	0.010	0.030	0.0				0.0	0.0				
1.13	0.122	0.019	0.010	0.029	0.0				0.0	0.0	23.33			
2.13	0.113	0.020	0.010	0.030	0.0				0.0	0.0				
3.13	0.103	0.022	0.011	0.033	0.0				0.0	0.0				
4.13	0.094	0.022	0.012	0.034	0.0				0.0	0.0	22.78			
5.13	0.086	0.024	0.012	0.036	0.0				0.02	0.16				
6.13	0.077	0.025	0.014	0.039	0.0				0.16	2.48				
7.13									0.40	14.00	23.33			
8.13									0.67	40.16				
9.13									0.91	82.28				
10.13									1.14	138.72	30.00			
11.13									0.90	205.20				
12.13									0.95	259.60				
13.13									1.29	319.32	33.33			
14.13									1.09	395.12				
15.13									0.37	454.76				
16.13									0.45	477.60	32.22			
17.13									0.27	503.16				
18.13									0.08	517.84				
19.13									0.01	522.08	27.78			
20.13									0.0	522.60				
21.13									0.0	522.60				
22.13									0.0	522.60	25.00			
23.13									0.0	522.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, METHYL DISULFIDE, 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 8-10-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.11 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.003				0.0				0.0	0.0				
1.30	0.003	0.003	0.009	0.012	0.0				0.0	0.0	21.67			
2.30	0.003	0.004	0.010	0.014	0.0				0.0	0.0				
3.30	0.0	0.788	0.003	0.791	0.0				0.0	0.0				
4.30	0.0	0.768	0.249	1.017	0.009				0.0	0.0	20.00			
5.30	0.0	0.749	0.256	1.005	0.007				0.01	0.18				
6.30	0.0	0.654	0.336	0.990	0.100				0.04	1.32				
7.30	0.0	0.325	0.569	0.894					0.11	4.98	20.00			
8.30	0.472	0.001	0.270	0.271	1.230				0.23	13.74		2.32	8.00	
9.30	0.629	0.002	0.056	0.058	1.052	0.006[a]	0.020	0.912	0.41	30.78				
10.30	0.548	0.003	0.030	0.033	0.953				0.69	60.42	25.56			
11.30	0.475	0.005	0.025	0.030	0.851				1.10	109.20				
12.30	0.421	0.007	0.024	0.031	0.759				1.03	173.94				
13.30	0.378	0.008	0.022	0.030	0.663				0.84	232.32	30.00			
14.30	0.346	0.009	0.021	0.030	0.579				0.73	280.74				
15.30	0.299	0.009	0.020	0.029	0.503				0.59	322.02				
16.30	0.266	0.008	0.019	0.027	0.428	0.009[a]	0.021	0.828	0.61	357.78	30.56			
17.30	0.233	0.009	0.018	0.027	0.370				0.28	388.44				
18.30	0.200	0.006	0.014	0.020	0.312				0.07	401.46				
19.30	0.153	0.005	0.014	0.019	0.225				0.02	404.76	27.22			
20.30	0.110	0.005	0.014	0.019	0.127				0.0	405.60				
21.30	0.077	0.003	0.015	0.018	0.060				0.0	405.60				
22.30	0.054	0.0	0.016	0.016	0.027				0.0	405.60	22.22			
23.30	0.038	0.010	0.015	0.025	0.013				0.0	405.60				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2,METHYL DISULFIDE, 95% DILUTION

DAY 2, 8-11-76
% POSSIBLE MINUTES SUNSHINE, 88
RDU AIRPORT MAXIMUM TEMPERATURE, 32.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.027	0.008	0.016	0.024	0.009				0.0	0.0				
1.30	0.019	0.007	0.016	0.023	0.006				0.0	0.0	18.89			
2.30	0.015	0.008	0.016	0.024	0.0				0.0	0.0				
3.30	0.008	0.008	0.015	0.023	0.0				0.0	0.0				
4.30	0.006	0.007	0.015	0.022	0.0				0.0	0.0	17.22			
5.30	0.003	0.006	0.015	0.021	0.0				0.01	0.18				
6.30	0.004	0.006	0.015	0.021	0.0				0.12	2.76				
7.30	0.017	0.012	0.016	0.028	0.0				0.36	14.28	19.44			
8.30	0.045	0.013	0.021	0.034	0.008				0.68	41.64				
9.30	0.091	0.018	0.019	0.037	0.017	0.100	0.018	0.370	0.93	86.94		2.32		8.00
10.30	0.136	0.009	0.023	0.032	0.021				1.12	146.16	27.78			
11.30	0.175	0.019	0.025	0.044	0.025				1.25	215.70				
12.30	0.201	0.010	0.030	0.040	0.026				1.28	291.24				
13.30	0.222	0.024	0.024	0.048	0.025				1.24	367.32	30.00			
14.30	0.234	0.022	0.027	0.049	0.030				0.87	435.06				
15.30	0.239	0.022	0.029	0.051	0.032				0.83	486.54				
16.30	0.241	0.023	0.026	0.049	0.027	0.091[a]	0.021	0.304	0.62	532.56	31.11			
17.30	0.235	0.020	0.024	0.044	0.030				0.32	564.36				
18.30	0.225	0.018	0.022	0.040	0.027				0.10	579.60				
19.30	0.206	0.018	0.018	0.036	0.024				0.0	583.80	25.00			
20.30	0.177	0.014	0.018	0.032	0.013				0.0	583.80				
21.30	0.150	0.011	0.017	0.028	0.007				0.0	583.80				
22.30	0.131	0.009	0.018	0.027	0.005				0.0	583.80	21.67			
23.30	0.117	0.008	0.017	0.025	0.0				0.0	583.80				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2,METHYL DISULFIDE, 95% DILUTION

DAY 3, 8-12-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.106	0.008	0.017	0.025	0.0				0.0	0.0				
1.30	0.096	0.007	0.016	0.023	0.0				0.0	0.0	20.56			
2.30	0.087	0.006	0.016	0.022	0.0				0.0	0.0				
3.30	0.080	0.006	0.016	0.022	0.0				0.0	0.0				
4.30	0.073	0.006	0.017	0.023	0.0				0.0	0.0	19.44			
5.30	0.067	0.006	0.017	0.023	0.0				0.02	0.36				
6.30	0.061	0.006	0.018	0.024	0.0				0.17	4.26				
7.30	0.059	0.011	0.023	0.034	0.0				0.44	19.32	21.67			
8.30	0.077	0.015	0.026	0.041	0.0				0.72	50.76				
9.30	0.113	0.017	0.024	0.041	0.0	0.134	0.017	0.248	0.98	98.64				
10.30	0.152	0.017	0.021	0.038	0.0				1.11	159.78	30.00			
11.30	0.179	0.016	0.019	0.035	0.007				1.25	228.90				
12.30	0.187	0.016	0.018	0.034	0.009				1.36	305.88				
13.30	0.209	0.016	0.016	0.032	0.009				1.23	385.14	32.22			
14.30	0.224	0.015	0.015	0.030	0.011				1.10	456.60				
15.30	0.225	0.017	0.016	0.033	0.009				0.87	518.46				
16.30	0.218	0.016	0.016	0.032	0.013				0.54	564.72	31.11			
17.30	0.214	0.015	0.015	0.030	0.011	0.196	0.020	0.179	0.29	592.62				
18.30	0.208	0.016	0.014	0.030	0.011				0.03	605.34				
19.30	0.199	0.017	0.012	0.029	0.009				0.01	606.78	27.78			
20.30	0.187	0.018	0.010	0.028	0.007				0.0	607.20				
21.30	0.169	0.019	0.010	0.029	0.005				0.0	607.20				
22.30	0.155	0.019	0.011	0.030	0.002				0.0	607.20	25.00			
23.30	0.143	0.020	0.012	0.032	0.0				0.0	607.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, METHYL DISULFIDE, 95% DILUTION

DAY 4, 8-13-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.132	0.021	0.013	0.034	0.0				0.0	0.0				
1.30	0.122	0.020	0.014	0.034	0.0				0.0	0.0	23.33			
2.30	0.113	0.020	0.015	0.035	0.0				0.0	0.0				
3.30	0.104	0.022	0.016	0.038	0.0				0.0	0.0				
4.30	0.096	0.022	0.018	0.040	0.0				0.0	0.0	22.78			
5.30	0.089	0.023	0.021	0.044	0.0				0.02	0.36				
6.30	0.083	0.024	0.024	0.048	0.0				0.16	4.08				
7.30									0.40	18.00	23.33			
8.30									0.67	46.86				
9.30									0.91	91.38				
10.30									1.14	150.12	30.00			
11.30									0.90	214.20				
12.30									0.95	269.10				
13.30									1.29	332.22	33.33			
14.30									1.09	406.02				
15.30									0.37	458.46				
16.30									0.45	482.10	32.22			
17.30									0.27	505.86				
18.30									0.08	518.64				
19.30									0.01	522.18	27.78			
20.30									0.0	522.60				
21.30									0.0	522.60				
22.30									0.0	522.60	25.00			
23.30									0.0	522.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 8-10-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.11 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.0				0.0				0.0	0.0				
1.47	0.0	0.001	0.003	0.004	0.0				0.0	0.0	21.67			
2.47	0.0	0.002	0.002	0.004	0.0				0.0	0.0				
3.47	0.0	0.802	0.0	0.802	0.0				0.0	0.0				
4.47	0.0	0.783	0.247	1.030	0.010				0.0	0.0	20.00			
5.47	0.0	0.770	0.246	1.016	0.009				0.01	0.28				
6.47	0.0	0.635	0.353	0.988	0.017				0.04	1.72				
7.47	0.181	0.003	0.698	0.701	0.084				0.11	6.08	20.00			
8.47	0.468	0.0	0.092	0.092	0.357				0.23	16.04		2.05	8.00	
9.47	0.404	0.0	0.034	0.034	0.338	0.119[a]	0.017	0.669	0.41	34.88				
10.47	0.318	0.0	0.024	0.024	0.301				0.69	67.32	25.56			
11.47	0.257	0.0	0.020	0.020	0.280				1.10	120.20				
12.47	0.218	0.0	0.018	0.018	0.245				1.03	184.24				
13.47	0.193	0.0	0.018	0.018	0.212				0.84	240.72	30.00			
14.47	0.172	0.0	0.015	0.015	0.178				0.73	288.04				
15.47	0.149	0.0	0.013	0.013	0.151				0.59	327.92				
16.47	0.133	0.0	0.013	0.013	0.125	0.099[a]	0.029	0.617	0.61	363.88	30.56			
17.47	0.117	0.001	0.012	0.013	0.101				0.28	391.24				
18.47	0.099	0.001	0.011	0.012	0.087				0.07	402.16				
19.47	0.079	0.003	0.010	0.013	0.069				0.02	404.96	27.22			
20.47	0.058	0.003	0.010	0.013	0.043				0.0	405.60				
21.47	0.040	0.001	0.010	0.011	0.016				0.0	405.60				
22.47	0.028	0.0	0.011	0.011	0.009				0.0	405.60	22.22			
23.47	0.020	0.009	0.010	0.019	0.007				0.0	405.60				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 95% DILUTION

DAY 2, 8-11-76
% POSSIBLE MINUTES SUNSHINE, 88
RDU AIRPORT MAXIMUM TEMPERATURE, 32.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.014	0.008	0.010	0.018	0.0				0.0	0.0				
1.47	0.009	0.008	0.010	0.018	0.0				0.0	0.0	18.89			
2.47	0.007	0.008	0.010	0.018	0.0				0.0	0.0				
3.47	0.005	0.007	0.010	0.017	0.0				0.0	0.0				
4.47	0.003	0.006	0.010	0.016	0.0				0.0	0.0	17.22			
5.47	0.002	0.006	0.010	0.016	0.0				0.01	0.28				
6.47	0.003	0.007	0.010	0.017	0.0				0.12	3.96				
7.47	0.016	0.012	0.011	0.023	0.0				0.36	17.88	19.44			
8.47	0.047	0.013	0.015	0.028	0.0				0.68	48.44		2.05		8.00
9.47	0.081	0.015	0.014	0.029	0.0	0.071	0.011	0.474	0.93	96.24				
10.47	0.109	0.016	0.018	0.034	0.008				1.12	157.36	27.78			
11.47	0.130	0.016	0.023	0.039	0.013				1.25	228.20				
12.47	0.146	0.006	0.029	0.035	0.014				1.28	304.04				
13.47	0.157	0.018	0.024	0.042	0.013				1.24	379.72	30.00			
14.47	0.164	0.017	0.028	0.045	0.011				0.87	443.76				
15.47	0.168	0.017	0.035	0.052	0.011				0.83	494.84				
16.47	0.169	0.015	0.028	0.043	0.011	0.071[a]	0.012	0.274	0.62	538.76	31.11			
17.47	0.164	0.014	0.024	0.038	0.011				0.32	567.56				
18.47	0.156	0.013	0.021	0.034	0.011				0.10	580.60				
19.47	0.149	0.013	0.019	0.032	0.006				0.0	583.80	25.00			
20.47	0.141	0.012	0.016	0.028	0.0				0.0	583.80				
21.47	0.128	0.010	0.014	0.024	0.0				0.0	583.80				
22.47	0.117	0.009	0.014	0.023	0.0				0.0	583.80	21.67			
23.47	0.108	0.008	0.014	0.022	0.0				0.0	583.80				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 95% DILUTION

DAY 3, 8-12-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.101	0.007	0.013	0.020	0.0				0.0	0.0				
1.47	0.094	0.007	0.012	0.019	0.0				0.0	0.0	20.56			
2.47	0.088	0.006	0.012	0.018	0.0				0.0	0.0				
3.47	0.084	0.006	0.012	0.018	0.0				0.0	0.0				
4.47	0.079	0.006	0.012	0.018	0.0				0.0	0.0	19.44			
5.47	0.074	0.006	0.012	0.018	0.0				0.02	0.56				
6.47	0.069	0.006	0.013	0.019	0.0				0.17	5.96				
7.47	0.068	0.010	0.018	0.028	0.0				0.44	23.72	21.67			
8.47	0.083	0.012	0.020	0.032	0.0				0.72	57.96				
9.47	0.108	0.013	0.019	0.032	0.0	0.112	0.012	0.299	0.98	108.44				
10.47	0.136	0.013	0.017	0.030	0.0				1.11	170.88	30.00			
11.47	0.152	0.013	0.016	0.029	0.0				1.25	241.40				
12.47	0.159	0.012	0.015	0.027	0.0				1.36	319.48				
13.47	0.175	0.012	0.015	0.027	0.006				1.23	397.44	32.22			
14.47	0.183	0.011	0.014	0.025	0.006				1.10	467.60				
15.47	0.180	0.012	0.015	0.027	0.004				0.87	527.16				
16.47	0.175	0.011	0.014	0.025	0.007				0.54	570.12	31.11			
17.47	0.169	0.010	0.013	0.023	0.004	0.156	0.025	0.256	0.29	595.52				
18.47	0.163	0.011	0.012	0.023	0.005				0.03	605.64				
19.47	0.156	0.013	0.011	0.024	0.0				0.01	606.88	27.78			
20.47	0.152	0.014	0.009	0.023	0.0				0.0	607.20				
21.47	0.147	0.016	0.008	0.024	0.0				0.0	607.20				
22.47	0.143	0.017	0.008	0.025	0.0				0.0	607.20	25.00			
23.47	0.138	0.019	0.007	0.026	0.0				0.0	607.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, METHYL SULFIDE , 95% DILUTION

DAY 4, 8-13-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.134	0.020	0.007	0.027	0.0				0.0	0.0				
1.47	0.128	0.020	0.007	0.027	0.0				0.0	0.0	23.33			
2.47	0.122	0.020	0.007	0.027	0.0				0.0	0.0				
3.47	0.116	0.021	0.008	0.029	0.0				0.0	0.0				
4.47	0.110	0.022	0.008	0.030	0.0				0.0	0.0	22.78			
5.47	0.105	0.023	0.008	0.031	0.0				0.02	0.56				
6.47	0.099	0.024	0.009	0.033	0.0				0.16	5.68				
7.47									0.40	22.00	23.33			
8.47									0.67	53.56				
9.47									0.91	100.48				
10.47									1.14	161.52	30.00			
11.47									0.90	223.20				
12.47									0.95	278.60				
13.47									1.29	345.12	33.33			
14.47									1.09	416.92				
15.47									0.37	462.16				
16.47									0.45	486.60	32.22			
17.47									0.27	508.56				
18.47									0.08	519.44				
19.47									0.01	522.28	27.78			
20.47									0.0	522.60				
21.47									0.0	522.60				
22.47									0.0	522.60	25.00			
23.47									0.0	522.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4,   PROPYLENE   , 95% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 8-10-76
% POSSIBLE MINUTES SUNSHINE, 83
RDU AIRPORT MAXIMUM TEMPERATURE, 31.11 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.001								0.0	0.0				
1.63	0.001	0.004	0.005	0.009					0.0	0.0	21.67			
2.63	0.001	0.005	0.006	0.011					0.0	0.0				
3.63	0.0	0.608	0.020	0.628					0.0	0.0				
4.63	0.0	0.707	0.154	0.861					0.0	0.0	20.00			
5.63	0.0	0.782	0.199	0.981					0.01	0.38				
6.63	0.0	0.730	0.246	0.976					0.04	2.12				
7.63	0.0	0.533	0.414	0.947					0.11	7.18	20.00			
8.63	0.018	0.111	0.726	0.837					0.23	18.34		2.30	8.00	
9.63	0.624	0.009	0.565	0.574					0.41	38.98				
10.63	0.951	0.008	0.363	0.371					0.69	74.22	25.56			
11.63	0.930	0.006	0.301	0.307					1.10	131.20				
12.63	0.927	0.003	0.253	0.256					1.03	194.54				
13.63	0.922	0.002	0.207	0.209					0.84	249.12	30.00			
14.63	0.879	0.001	0.167	0.168					0.73	295.34				
15.63	0.798	0.0	0.138	0.138					0.59	333.82				
16.63	0.723	0.0	0.115	0.115		0.042	0.131	0.445	0.61	369.98	30.56			
17.63	0.650	0.0	0.095	0.095					0.28	394.04				
18.63	0.573	0.0	0.076	0.076					0.07	402.86				
19.63	0.500	0.0	0.065	0.065					0.02	405.16	27.22			
20.63	0.443	0.0	0.057	0.057					0.0	405.60				
21.63	0.386	0.0	0.048	0.048					0.0	405.60				
22.63	0.347	0.0	0.044	0.044					0.0	405.60	22.22			
23.63	0.301	0.008	0.039	0.047					0.0	405.60				

RTI SMOG CHAMBER STUDY; USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4,   PROPYLENE   , 95% DILUTION

DAY 2, 8-11-76
% POSSIBLE MINUTES SUNSHINE, 88
RDU AIRPORT MAXIMUM TEMPERATURE, 32.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NEKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.263	0.007	0.035	0.042					0.0	0.0				
1.63	0.231	0.006	0.033	0.039					0.0	0.0	18.89			
2.63	0.201	0.006	0.030	0.036					0.0	0.0				
3.63	0.176	0.006	0.028	0.034					0.0	0.0				
4.63	0.154	0.006	0.027	0.033					0.0	0.0	17.22			
5.63	0.132	0.006	0.026	0.032					0.01	0.38				
6.63	0.115	0.006	0.025	0.031					0.12	5.16				
7.63	0.108	0.010	0.030	0.040					0.36	21.48	19.44			
8.63	0.127	0.010	0.033	0.043					0.68	55.24		2.30		8.00
9.63	0.170	0.012	0.034	0.046		0.183	0.020	0.553	0.93	105.54				
10.63	0.219	0.012	0.038	0.050					1.12	168.56	27.78			
11.63	0.261	0.012	0.042	0.054					1.25	240.70				
12.63	0.290	0.012	0.046	0.058					1.28	316.84				
13.63	0.307	0.014	0.038	0.052					1.24	392.12	30.00			
14.63	0.314	0.013	0.042	0.055					0.87	452.46				
15.63	0.310	0.013	0.049	0.062					0.83	503.14				
16.63	0.302	0.012	0.040	0.052		0.154	0.017	0.525	0.62	544.96	31.11			
17.63	0.286	0.011	0.034	0.045					0.32	570.76				
18.63	0.274	0.010	0.030	0.040					0.10	581.60				
19.63	0.264	0.011	0.025	0.036					0.0	583.80	25.00			
20.63	0.256	0.011	0.022	0.033					0.0	583.80				
21.63	0.248	0.010	0.020	0.030					0.0	583.80				
22.63	0.238	0.008	0.019	0.027					0.0	583.80	21.67			
23.63	0.230	0.008	0.018	0.026					0.0	583.80				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 95% DILUTION

DAY 3, 8-12-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (LST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.222	0.007	0.017	0.024					0.0	0.0				
1.63	0.214	0.007	0.016	0.023					0.0	0.0	20.56			
2.63	0.207	0.006	0.015	0.021					0.0	0.0				
3.63	0.200	0.006	0.015	0.021					0.0	0.0				
4.63	0.194	0.006	0.014	0.020					0.0	0.0	19.44			
5.63	0.186	0.006	0.014	0.020					0.02	0.76				
6.63	0.179	0.006	0.016	0.022					0.17	7.66				
7.63	0.171	0.010	0.020	0.030					0.44	28.12	21.67			
8.63	0.171	0.010	0.023	0.033					0.72	65.16				
9.63	0.184	0.011	0.024	0.035		0.194	0.015	0.528	0.98	118.24				
10.63	0.206	0.011	0.023	0.034					1.11	181.98	30.00			
11.63	0.217	0.011	0.022	0.033					1.25	253.90				
12.63	0.224	0.010	0.022	0.032					1.36	333.08				
13.63	0.245	0.010	0.022	0.032					1.23	409.74	32.22			
14.63	0.246	0.010	0.021	0.031					1.10	478.60				
15.63	0.236	0.010	0.020	0.030					0.87	535.86				
16.63	0.227	0.010	0.020	0.030					0.54	575.52	31.11			
17.63	0.219	0.009	0.018	0.027		0.267	0.026	0.413	0.29	598.42				
18.63	0.209	0.010	0.016	0.026					0.03	605.94				
19.63	0.202	0.011	0.014	0.025					0.01	606.98	27.78			
20.63	0.196	0.013	0.013	0.026					0.0	607.20				
21.63	0.192	0.015	0.011	0.026					0.0	607.20				
22.63	0.186	0.017	0.010	0.027					0.0	607.20	25.00			
23.63	0.183	0.018	0.010	0.028					0.0	607.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 95% DILUTION

DAY 4, 8-13-76
% POSSIBLE MINUTES SUNSHINE, 66
RDU AIRPORT MAXIMUM TEMPERATURE, 33.33 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	* DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.178	0.018	0.009	0.027					0.0	0.0				
1.63	0.174	0.018	0.009	0.027					0.0	0.0	23.33			
2.63	0.170	0.019	0.008	0.027					0.0	0.0				
3.63	0.166	0.020	0.008	0.028					0.0	0.0				
4.63	0.163	0.022	0.008	0.030					0.0	0.0	22.78			
5.63	0.157	0.022	0.008	0.030					0.02	0.76				
6.63	0.152	0.024	0.009	0.033					0.16	7.28				
7.63									0.40	26.00	23.33			
8.63									0.67	60.26				
9.63									0.91	109.58				
10.63									1.14	172.92	30.00			
11.63									0.90	232.20				
12.63									0.95	288.10				
13.63									1.29	358.02	33.33			
14.63									1.09	427.82				
15.63									0.37	465.86				
16.63									0.45	491.10	32.22			
17.63									0.27	511.26				
18.63									0.08	520.24				
19.63									0.01	522.38	27.78			
20.63									0.0	522.60				
21.63									0.0	522.60				
22.63									0.0	522.60	25.00			
23.63									0.0	522.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1,   FURAN   , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 8-17-76
% POSSIBLE MINUTES SUNSHINE, 91
RDU AIRPORT MAXIMUM TEMPERATURE, 27.78 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBK1 (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.0								0.0	0.0				
1.13	0.0	0.010	0.007	0.017					0.0	0.0	21.11			
2.13	0.0	0.010	0.008	0.018					0.0	0.0				
3.13	0.0	0.011	0.164	0.175					0.0	0.0				
4.13	0.0	0.726	0.235	0.961					0.0	0.0	18.89			
5.13	0.0								0.01	0.08				
6.13	0.0	0.690	0.266	0.956					0.12	1.56				
7.13	0.0	0.621	0.320	0.941					0.39	10.92	19.44			
8.13	0.007	0.194	0.652	0.846					0.57	35.76				
9.13	0.506								0.87	72.36				
10.13	0.507	0.011	0.119	0.130		0.696	0.041	0.098	1.18	127.04	23.89			
11.13	0.476	0.012	0.093	0.105					1.29	198.72				
12.13	0.448	0.011	0.080	0.091					1.34	276.52				
13.13	0.425	0.016	0.067	0.083					1.26	356.28	26.11			
14.30	0.392	0.013	0.063	0.076					1.13	442.14				
15.13	0.378	0.015	0.053	0.068		0.454	0.017	0.0	0.91	496.88				
16.13	0.356	0.014	0.048	0.062					0.64	549.32	27.78			
17.13	0.330	0.011	0.045	0.056					0.34	585.32				
18.13	0.303	0.011	0.040	0.051					0.06	603.48				
19.13	0.272	0.006	0.032	0.038					0.0	606.60	23.89			
20.13	0.252	0.005	0.028	0.033					0.0	606.60				
21.13	0.248	0.004	0.027	0.031					0.0	606.60				
22.13	0.225	0.003	0.026	0.029					0.0	606.60	17.78			
23.13	0.213	0.004	0.026	0.030					0.0	606.60				

RTI SMOG CHAMBER STUDY; USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 0% DILUTION

PAGE 2

DAY 2, 8-18-76
% POSSIBLE MINUTES SUNSHINE, 93
RDU AIRPORT MAXIMUM TEMPERATURE, 29.44 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.201	0.002	0.023	0.025					0.0	0.0				
1.13	0.192	0.002	0.023	0.025					0.0	0.0	16.67			
2.13	0.181	0.002	0.022	0.024					0.0	0.0				
3.13	0.172	0.002	0.022	0.024					0.0	0.0				
4.13	0.163	0.002	0.021	0.023					0.0	0.0	14.44			
5.13	0.154	0.001	0.020	0.021					0.01	0.08				
6.13	0.146	0.001	0.021	0.022					0.15	1.80				
7.13	0.132	0.003	0.022	0.025					0.47	13.36	17.78			
8.13	0.122	0.006	0.029	0.035					0.72	43.56				
9.13	0.123	0.010	0.032	0.042					0.97	88.76				
10.13	0.141	0.012	0.033	0.045		0.179	0.017	0.011	1.18	148.64	25.56			
11.13	0.161	0.013	0.032	0.045					1.32	220.56				
12.13	0.182	0.011	0.027	0.038					1.32	299.76				
13.13	0.199	0.013	0.027	0.040					1.10	377.20	27.78			
14.13	0.206	0.014	0.026	0.040					1.02	442.56				
15.13	0.208	0.013	0.026	0.039		0.258	0.013	0.023	0.86	502.48				
16.13	0.204	0.011	0.024	0.035					0.55	551.60	28.33			
17.13	0.195	0.010	0.023	0.033					0.28	582.44				
18.13	0.181	0.018	0.021	0.039					0.07	597.56				
19.13	0.167	0.019	0.016	0.035					0.0	601.20	24.44			
20.13	0.151	0.018	0.015	0.033					0.0	601.20				
21.13	0.140	0.016	0.014	0.030					0.0	601.20				
22.13	0.130	0.016	0.014	0.030					0.0	601.20	21.11			
23.13	0.122	0.014	0.014	0.028					0.0	601.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 1, FURAN , 0% DILUTION

DAY 3, 8-19-76
% POSSIBLE MINUTES SUNSHINE, 92
RDU AIRPORT MAXIMUM TEMPERATURE, 27.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.13	0.113	0.014	0.015	0.029					0.0	0.0				
1.13	0.105	0.011	0.014	0.025					0.0	0.0	18.89			
2.13	0.099	0.010	0.015	0.025					0.0	0.0				
3.13	0.093	0.010	0.015	0.025					0.0	0.0				
4.13	0.086	0.009	0.015	0.024					0.0	0.0	15.56			
5.13	0.079								0.01	0.08				
6.13	0.073	0.0	0.018	0.018					0.15	1.80				
7.13	0.065	0.0	0.018	0.018					0.45	13.20	17.22			
8.13	0.070	0.0	0.021	0.021					0.69	42.12				
9.13	0.084	0.0	0.020	0.020					1.07	86.56				
10.13	0.107	0.0	0.025	0.025		0.133	0.015	0.040	1.15	151.40	23.33			
11.13	0.121	0.0	0.020	0.020					1.22	220.96				
12.13	0.148	0.0	0.024	0.024					1.36	295.28				
13.13	0.166	0.0	0.020	0.020					1.41	377.28	26.11			
14.13	0.172	0.0	0.025	0.025		0.216	0.014	0.037	0.90	457.80				
15.13	0.170	0.0	0.020	0.020					0.56	509.08				
16.13	0.157	0.0	0.023	0.023					0.46	541.88	25.00			
17.13	0.153	0.0	0.021	0.021					0.29	568.12				
18.13		0.0	0.024	0.024					0.04	583.52				
19.13	0.142	0.0	0.020	0.020					0.01	585.68	22.78			
20.13									0.0	586.20				
21.13									0.0	586.20				
22.13									0.0	586.20	20.00			
23.13									0.0	586.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2256

CHAMBER NO. 2, THIOPHENE , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

PAGE 1

DAY 1, 8-17-76
% POSSIBLE MINUTES SUNSHINE, 91
RDU AIRPORT MAXIMUM TEMPERATURE, 27.78 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.004	0.003	0.008	0.011	0.0				0.0	0.0				
1.30	0.003	0.008	0.009	0.017	0.0				0.0	0.0	21.11			
2.30	0.003	0.009	0.008	0.017	0.0				0.0	0.0				
3.30	0.003	0.010	0.226	0.236	0.0				0.0	0.0				
4.30	0.0	0.741	0.235	0.976	0.0				0.0	0.0	18.89			
5.30	0.0				0.0				0.01	0.18				
6.30	0.0	0.717	0.270	0.987	0.009				0.12	2.76				
7.30	0.0	0.690	0.289	0.979	0.012				0.39	14.82	19.44			
8.30	0.0	0.621	0.324	0.945	0.025				0.57	41.46				
9.30	0.0	0.553	0.358	0.911	0.035				0.87	81.06				
10.30	0.0	0.447	0.392	0.839	0.063	0.021	0.449	0.025	1.18	138.84	23.89			
11.30	0.001	0.366	0.387	0.753	0.092				1.29	211.62				
12.30	0.002	0.301	0.383	0.684	0.122				1.34	289.92				
13.30	0.003	0.251	0.375	0.626	0.153				1.26	368.88	26.11			
14.47	0.005	0.202	0.360	0.562	0.182				1.13	453.44				
15.30	0.007	0.177	0.336	0.513	0.202	0.018	0.463	0.0	0.91	505.98				
16.30	0.007	0.156	0.317	0.473	0.223				0.64	555.72	27.78			
17.30	0.006	0.141	0.290	0.[illegible]31	0.227				0.34	588.72				
18.30	0.001	0.134	0.283	0.[illegible]7	0.206				0.06	604.08				
19.30	0.0	0.125	0.289	0.414	0.156				0.0	606.60	23.89			
20.30	0.0	0.129	0.299	0.428	0.107				0.0	606.60				
21.30	0.0	0.130	0.296-	0.426	0.089				0.0	606.60				
22.30	0.0	0.131	0.288	0.419	0.072				0.0	606.60	17.78			
23.30	0.0	0.130	0.280	0.410	0.052				0.0	606.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 0% DILUTION PAGE 2

DAY 2, 8-18-76
% POSSIBLE MINUTES SUNSHINE, 93
RDU AIRPORT MAXIMUM TEMPERATURE, 29.44 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.0	0.132	0.272	0.404	0.041				0.0	0.0				
1.30	0.0	0.134	0.266	0.400	0.034				0.0	0.0	16.67			
2.30	0.0	0.136	0.259	0.395	0.028				0.0	0.0				
3.30	0.0	0.137	0.255	0.392	0.022				0.0	0.0				
4.30	0.0	0.139	0.250	0.389	0.018				0.0	0.0	14.44			
5.30	0.0	0.138	0.248	0.386	0.017				0.01	0.18				
6.30	0.0	0.139	0.240	0.379	0.017				0.15	3.30				
7.30	0.002	0.125	0.209	0.334	0.038				0.47	18.06	17.78			
8.30	0.009	0.109	0.189	0.298	0.071				0.72	50.76				
9.30	0.016	0.086	0.176	0.262	0.090				0.97	98.46				
10.30	0.032	0.061	0.169	0.230	0.113	0.008[a]	0.239	0.052	1.18	160.44	25.56			
11.30	0.053	0.044	0.150	0.194	0.141				1.32	233.76				
12.30	0.079	0.031	0.129	0.160	0.161				1.32	312.96				
13.30	0.102	0.027	0.111	0.138	0.173				1.10	388.20	27.78			
14.30	0.118	0.023	0.095	0.118	0.181				1.02	452.76				
15.30	0.130	0.020	0.078	0.098	0.187	0.003[a]	0.094	0.034	0.86	511.08				
16.30	0.132	0.018	0.068	0.086	0.191				0.55	557.10	28.33			
17.30	0.122	0.014	0.061	0.075	0.179				0.28	585.24				
18.30	0.101	0.022	0.054	0.076	0.159				0.07	598.26				
19.30	0.072	0.020	0.045	0.065	0.114				0.0	601.20	24.44			
20.30	0.050	0.018	0.038	0.056	0.084				0.0	601.20				
21.30	0.033	0.017	0.035	0.052	0.058				0.0	601.20				
22.30	0.022	0.016	0.034	0.050	0.046				0.0	601.20	21.11			
23.30	0.015	0.014	0.034	0.048	0.031				0.0	601.20				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 2, THIOPHENE , 0% DILUTION

DAY 3, 8-19-76
% POSSIBLE MINUTES SUNSHINE, 92
RDU AIRPORT MAXIMUM TEMPERATURE, 32.78 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.30	0.010	0.013	0.033	0.046	0.024				0.0	0.0				
1.30	0.005	0.010	0.033	0.043	0.020				0.0	0.0	18.89			
2.30	0.002	0.010	0.032	0.042	0.010				0.0	0.0				
3.30	0.001	0.010	0.032	0.042	0.009				0.0	0.0				
4.30	0.0	0.010	0.033	0.043	0.008				0.0	0.0	15.56			
5.30	0.0				0.007				0.01	0.18				
6.30	0.002	0.0	0.036	0.036	0.005				0.15	3.30				
7.30	0.020	0.0	0.028	0.028	0.016				0.45	17.70	17.22			
8.30	0.051	0.0	0.026	0.026	0.018				0.69	49.02				
9.30	0.063	0.0	0.023	0.023	0.021				1.07	97.26				
10.30	0.097	0.0	0.023	0.023	0.025	0.052[a]	0.021	0.062	1.15	162.90	23.33			
11.30	0.115	0.0	0.021	0.021	0.028				1.22	233.16				
12.30	0.143	0.0	0.022	0.022	0.029				1.36	308.88				
13.30	0.164	0.0	0.021	0.021	0.035				1.41	391.38	26.11			
14.30	0.173	0.0	0.023	0.023	0.034	0.170[a]	0.014	0.045	0.90	466.80				
15.30	0.165	0.0	0.020	0.020	0.033				0.56	514.68				
16.30	0.145	0.0	0.022	0.022	0.030				0.46	546.48	25.00			
17.30	0.153	0.0	0.021	0.021	0.026				0.29	571.02				
18.30	0.148	0.0	0.024	0.024	0.022				0.04	583.92				
19.30	0.139	0.0	0.021	0.021	0.016				0.01	585.78	22.78			
20.30									0.0	586.20				
21.30									0.0	586.20				
22.30									0.0	586.20	20.00			
23.30									0.0	586.20				

[a] This NBKI measurement may be low in comparison to the chemiluminescent ozone reading due to the negative interference of sulfur dioxide on the NBKI measurement.

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3,   PYRROLE   , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

DAY 1, 8-17-76
% POSSIBLE MINUTES SUNSHINE, 91
RDU AIRPORT MAXIMUM TEMPERATURE, 27.78 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.0	0.004	0.006	0.010					0.0	0.0				
1.47	0.0	0.009	0.007	0.016					0.0	0.0	21.11			
2.47	0.0	0.009	0.008	0.017					0.0	0.0				
3.47	0.0	0.010	0.233	0.243					0.0	0.0				
4.47	0.0	0.711	0.232	0.943					0.0	0.0	18.89			
5.47	0.0	0.704	0.231	0.935					0.01	0.28				
6.47	0.0	0.626	0.286	0.912					0.12	3.96				
7.47	0.0	0.363	0.493	0.856					0.39	18.72	19.44			
8.47	0.025	0.078	0.551	0.629					0.57	47.16				
9.47	0.013	0.111	0.413	0.524		0.086	0.372	0.056	0.87	89.76				
10.47	0.008	0.139	0.333	0.472					1.18	150.64	23.89			
11.47	0.006	0.141	0.278	0.419					1.29	224.52				
12.47	0.007	0.139	0.244	0.383					1.34	303.32				
13.47	0.009	0.122	0.221	0.343					1.26	381.48	26.11			
14.63	0.010	0.100	0.199	0.299					1.13	464.74				
15.47	0.012	0.085	0.182	0.267		0.037		0.0	0.91	515.08				
16.47	0.013	0.072	0.166	0.238					0.64	562.12	27.78			
17.47	0.011	0.060	0.157	0.217					0.34	592.12				
18.47	0.003	0.046	0.150	0.196					0.06	604.68				
19.47	0.0	0.036	0.156	0.192					0.0	606.60	23.89			
20.47	0.0	0.037	0.165	0.202					0.0	606.60				
21.47	0.0	0.036	0.163	0.199					0.0	606.60				
22.47	0.0	0.034	0.160	0.194					0.0	606.60	17.78			
23.47	0.0	0.033	0.154	0.187					0.0	606.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3,   PYRROLE   , 0% DILUTION

DAY 2, 8-18-76
% POSSIBLE MINUTES SUNSHINE, 91
RDU AIRPORT MAXIMUM TEMPERATURE, 29.44 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.0	0.034	0.151	0.185					0.0	0.0				
1.47	0.0	0.035	0.149	0.184					0.0	0.0	16.67			
2.47	0.0	0.035	0.145	0.180					0.0	0.0				
3.47	0.0	0.036	0.142	0.178					0.0	0.0				
4.47	0.0	0.035	0.139	0.174					0.0	0.0	14.44			
5.47	0.0	0.034	0.137	0.171					0.01	0.28				
6.47	0.003	0.037	0.128	0.165					0.15	4.80				
7.47	0.011	0.041	0.104	0.145					0.47	22.76	17.78			
8.47	0.014	0.047	0.088	0.135					0.72	57.96				
9.47	0.018	0.046	0.081	0.127					0.97	108.16				
10.47	0.028	0.037	0.076	0.113		0.043	0.090	0.010	1.18	172.24	25.56			
11.47	0.042	0.030	0.069	0.099					1.32	246.96				
12.47	0.057	0.023	0.058	0.081					1.32	326.16				
13.47	0.073	0.022	0.053	0.075					1.10	399.20	27.78			
14.47	0.086	0.020	0.046	0.066					1.02	462.96				
15.47	0.096	0.019	0.040	0.059		0.113	0.039	0.023	0.86	519.68				
16.47	0.100	0.014	0.035	0.049					0.55	562.60	28.33			
17.47	0.097	0.013	0.032	0.045					0.28	588.04				
18.47	0.087	0.021	0.028	0.049					0.07	598.96				
19.47	0.074	0.020	0.024	0.044					0.0	601.20	24.44			
20.47	0.065	0.018	0.020	0.038					0.0	601.20				
21.47	0.056	0.017	0.017	0.034					0.0	601.20				
22.47	0.050	0.015	0.016	0.031					0.0	601.20	21.11			
23.47	0.045	0.014	0.014	0.028					0.0	601.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 3, PYRROLE , 0% DILUTION PAGE 3

DAY 3, 8-19-76
% POSSIBLE MINUTES SUNSHINE, 92
RDU AIRPORT MAXIMUM TEMPERATURE, 27.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.47	0.040	0.012	0.015	0.027					0.0	0.0				
1.47	0.036	0.009	0.014	0.023					0.0	0.0	18.89			
2.47	0.032	0.010	0.013	0.023					0.0	0.0				
3.47	0.028	0.010	0.014	0.024					0.0	0.0				
4.47	0.024	0.009	0.014	0.023					0.0	0.0	15.56			
5.47	0.022								0.01	0.28				
6.47	0.020	0.0	0.020	0.020					0.15	4.80				
7.47	0.024	0.0	0.016	0.016					0.45	22.20	17.22			
8.47	0.046	0.0	0.014	0.014					0.69	55.92				
9.47	0.060	0.0	0.014	0.014					1.07	107.96				
10.47	0.084	0.0	0.017	0.017		0.080	0.010	0.044	1.15	174.40	23.33			
11.47	0.100	0.0	0.015	0.015					1.22	245.36				
12.47	0.121	0.0	0.016	0.016					1.36	322.48				
13.47	0.136	0.0	0.016	0.016					1.41	405.48	26.11			
14.47	0.136	0.0	0.017	0.017		0.151	0.009	0.0	0.90	475.80				
15.47	0.130	0.0	0.015	0.015					0.56	520.28				
16.47	0.122	0.0	0.018	0.018					0.46	551.08	25.00			
17.47	0.120	0.0	0.016	0.016					0.29	573.92				
18.47	0.115	0.0	0.020	0.020					0.04	584.32				
19.47	0.111	0.0	0.018	0.018					0.01	585.88	22.78			
20.47									0.0	586.20				
21.47									0.0	586.20				
22.47									0.0	586.20	20.00			
23.47									0.0	586.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION
TARGET INITIAL HC/NOX: 5.0 PPMC/1.00 PPM

PAGE 1

DAY 1, 8-17-76
% POSSIBLE MINUTES SUNSHINE, 91
RDU AIRPORT MAXIMUM TEMPERATURE, 27.78 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.0	0.004	0.004	0.008					0.0	0.0				
1.63	0.0	0.008	0.005	0.013					0.0	0.0	21.11			
2.63	0.0	0.004	0.008	0.012					0.0	0.0				
3.63	0.0	0.008	0.197	0.205					0.0	0.0				
4.63	0.0	0.282	0.203	0.485					0.0	0.0	18.89			
5.63	0.0	0.648	0.215	0.863					0.01	0.38				
6.63	0.0	0.599	0.260	0.859					0.12	5.16				
7.63	0.0	0.409	0.432	0.841					0.39	22.62	19.44			
8.63	0.098	0.022	0.744	0.766					0.57	52.86				
9.63	0.737	0.010	0.467	0.477		1.356	0.083	0.963	0.87	98.46				
10.63	0.899	0.012	0.370	0.382					1.18	162.44	23.89			
11.63	0.877	0.012	0.348	0.360					1.29	237.42				
12.63	0.901	0.011	0.329	0.340					1.34	316.72				
13.63	0.946	0.012	0.302	0.314					1.26	394.08	26.11			
14.80	0.965	0.010	0.276	0.286					1.13	476.04				
15.63	0.969	0.010	0.255	0.265		1.367	0.027	0.339	0.91	524.18				
16.63	0.943	0.009	0.232	0.241					0.64	568.52	27.78			
17.63	0.906	0.007	0.216	0.223					0.34	595.52				
18.63	0.866	0.003	0.193	0.196					0.06	605.28				
19.63	0.821	0.0	0.179	0.179					0.0	606.60	23.89			
20.63	0.799	0.0	0.175	0.175					0.0	606.60				
21.63	0.775	0.0	0.167	0.167					0.0	606.60				
22.63	0.760	0.002	0.163	0.165					0.0	606.60	17.78			
23.63	0.740	0.002	0.160	0.162					0.0	606.60				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION

DAY 2, 8-18-76
% POSSIBLE MINUTES SUNSHINE, 93
RDU AIRPORT MAXIMUM TEMPERATURE, 29.44 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.722	0.002	0.152	0.154					0.0	0.0				
1.63	0.704	0.002	0.148	0.150					0.0	0.0	16.67			
2.63	0.693	0.002	0.145	0.147					0.0	0.0				
3.63	0.680	0.002	0.144	0.146					0.0	0.0				
4.63	0.667	0.002	0.141	0.143					0.0	0.0	14.44			
5.63	0.652	0.001	0.136	0.137					0.01	0.38				
6.63	0.641	0.001	0.132	0.133					0.15	6.30				
7.63	0.632	0.001	0.135	0.136					0.47	27.46	17.78			
8.63	0.613	0.006	0.143	0.149					0.72	65.16				
9.63	0.609	0.008	0.140	0.148		0.871	0.019	0.263	0.97	117.86				
10.63	0.621	0.010	0.132	0.142					1.18	184.04	25.56			
11.63	0.648	0.010	0.123	0.133					1.32	260.16				
12.63	0.675	0.008	0.110	0.118					1.32	339.36				
13.63	0.694	0.010	0.103	0.113					1.10	410.20	27.78			
14.63	0.698	0.011	0.094	0.105		0.918	0.018	0.097	1.02	473.16				
15.63	0.689	0.011	0.085	0.096					0.86	528.28				
16.63	0.668	0.009	0.076	0.085					0.55	568.10	28.33			
17.63	0.640	0.008	0.068	0.076					0.28	590.84				
18.63	0.617	0.016	0.059	0.075					0.07	599.66				
19.63	0.598	0.016	0.053	0.069					0.0	601.20	24.44			
20.63	0.580	0.015	0.049	0.064					0.0	601.20				
21.63	0.563	0.014	0.044	0.058					0.0	601.20				
22.63	0.548	0.013	0.042	0.055					0.0	601.20	21.11			
23.63	0.532	0.012	0.040	0.052					0.0	601.20				

RTI SMOG CHAMBER STUDY: USEPA CONTRACT NO. 68-02-2258

CHAMBER NO. 4, PROPYLENE , 0% DILUTION

DAY 3, 8-19-76
% POSSIBLE MINUTES SUNSHINE, 92
RDU AIRPORT MAXIMUM TEMPERATURE, 27.22 CENT

TIME (EST)	OZONE (PPM)	NO (PPM)	NO2 (PPM)	NOX (PPM)	SO2 (PPM)	NBKI (PPM)	NO2-S (PPM)	CH2O (PPM)	SR (LANG /MIN)	CUM-SR (LANG)	TEMP (CENT)	DILUTION (CFM)	BEGAN (EST)	ENDED (EST)
0.63	0.519	0.010	0.038	0.048					0.0	0.0				
1.63	0.503	0.008	0.036	0.044					0.0	0.0				
2.63	0.492	0.008	0.035	0.043					0.0	0.0	18.89			
3.63	0.480	0.008	0.034	0.042					0.0	0.0				
4.63	0.470	0.008	0.033	0.041					0.0	0.0				
5.63	0.460	0.0	0.036	0.036					0.01	0.38	15.56			
6.63	0.447	0.0	0.038	0.038					0.15	6.30				
7.63	0.432	0.0	0.036	0.036					0.45	26.70				
8.63	0.404	0.0	0.039	0.039					0.69	62.82	17.22			
9.63	0.398	0.0	0.040	0.040					1.07	118.66				
10.63	0.377	0.0	0.040	0.040		0.511	0.011	0.101	1.15	185.90				
11.63	0.381	0.0	0.039	0.039					1.22	257.56	23.33			
12.63	0.389	0.0	0.040	0.040					1.36	336.08				
13.63	0.400	0.0	0.038	0.038					1.41	419.58				
14.63	0.387	0.0	0.037	0.037					0.90	484.80	26.11			
15.63	0.375	0.0	0.035	0.035		0.476	0.013	0.063	0.56	525.88				
16.63	0.353	0.0	0.037	0.037					0.46	555.68				
17.63	0.350	0.0	0.032	0.032					0.29	576.82	25.00			
18.63	0.341	0.0	0.032	0.032					0.04	584.72				
19.63	0.338	0.0	0.028	0.028					0.01	585.98				
20.63									0.0	586.20	22.78			
21.63									0.0	586.20				
22.63									0.0	586.20				
23.63									0.0	586.20	20.00			

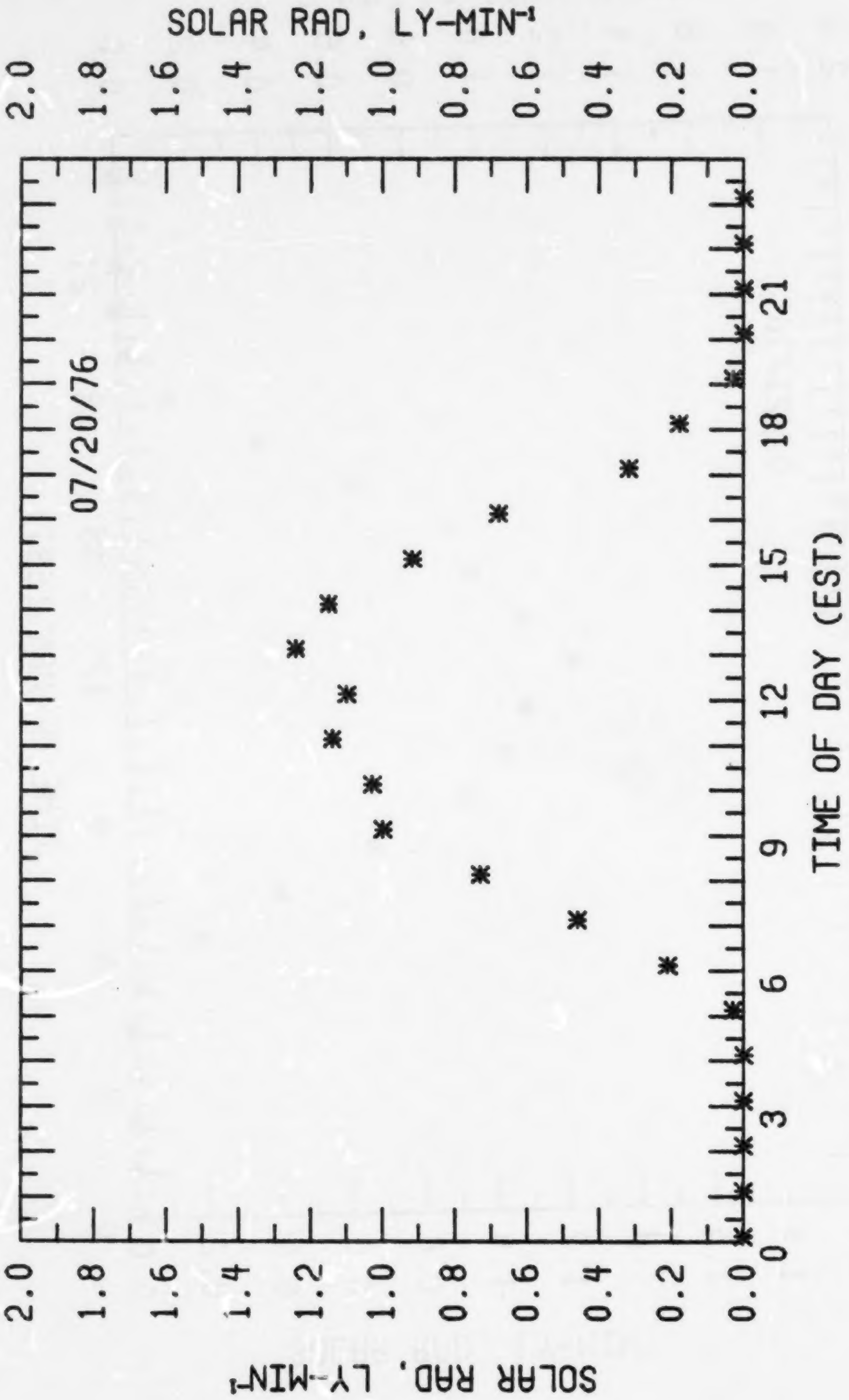
APPENDIX E

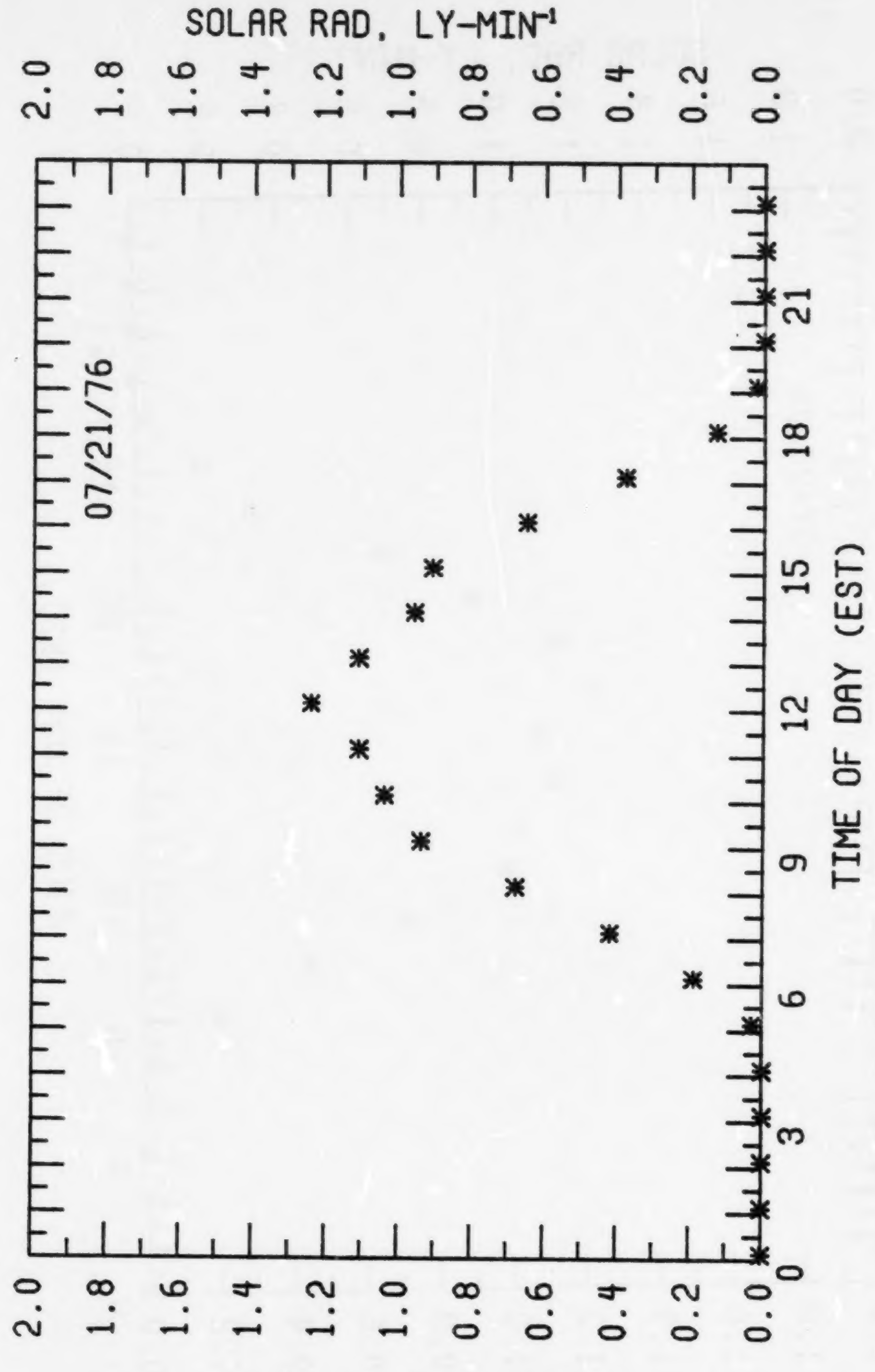
Concentration Profiles

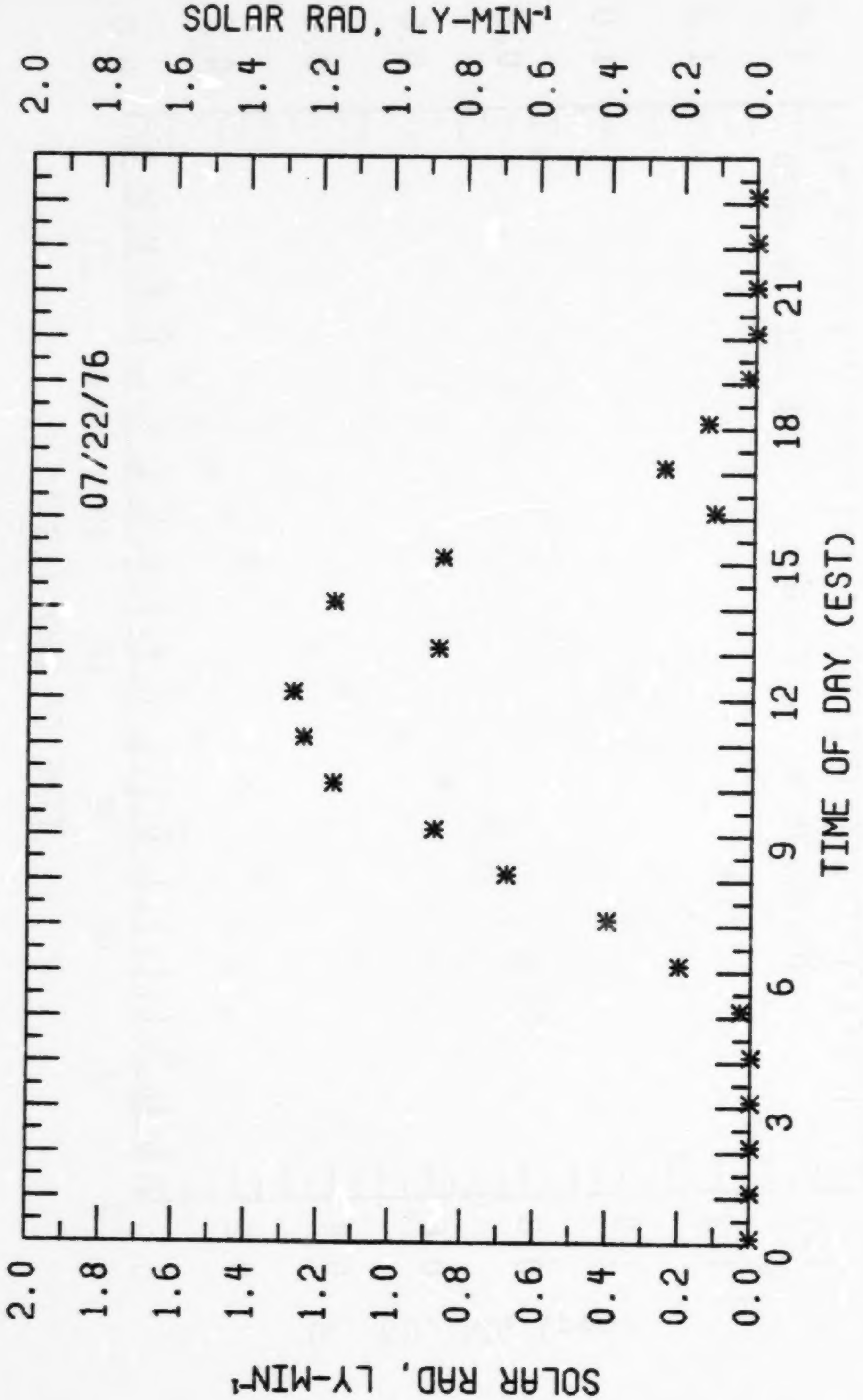
Appendix E. CONCENTRATION PROFILES

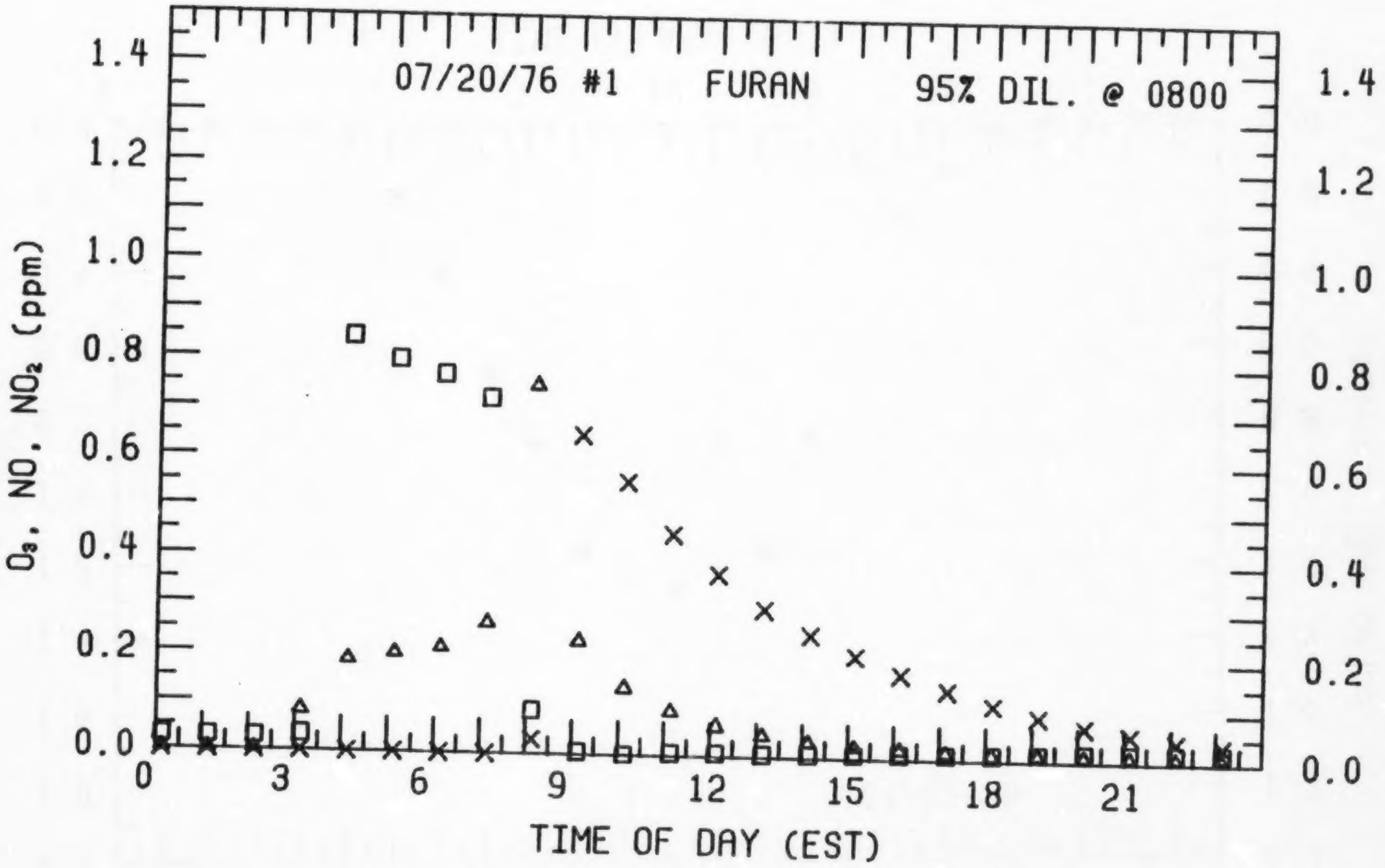
Symbols:

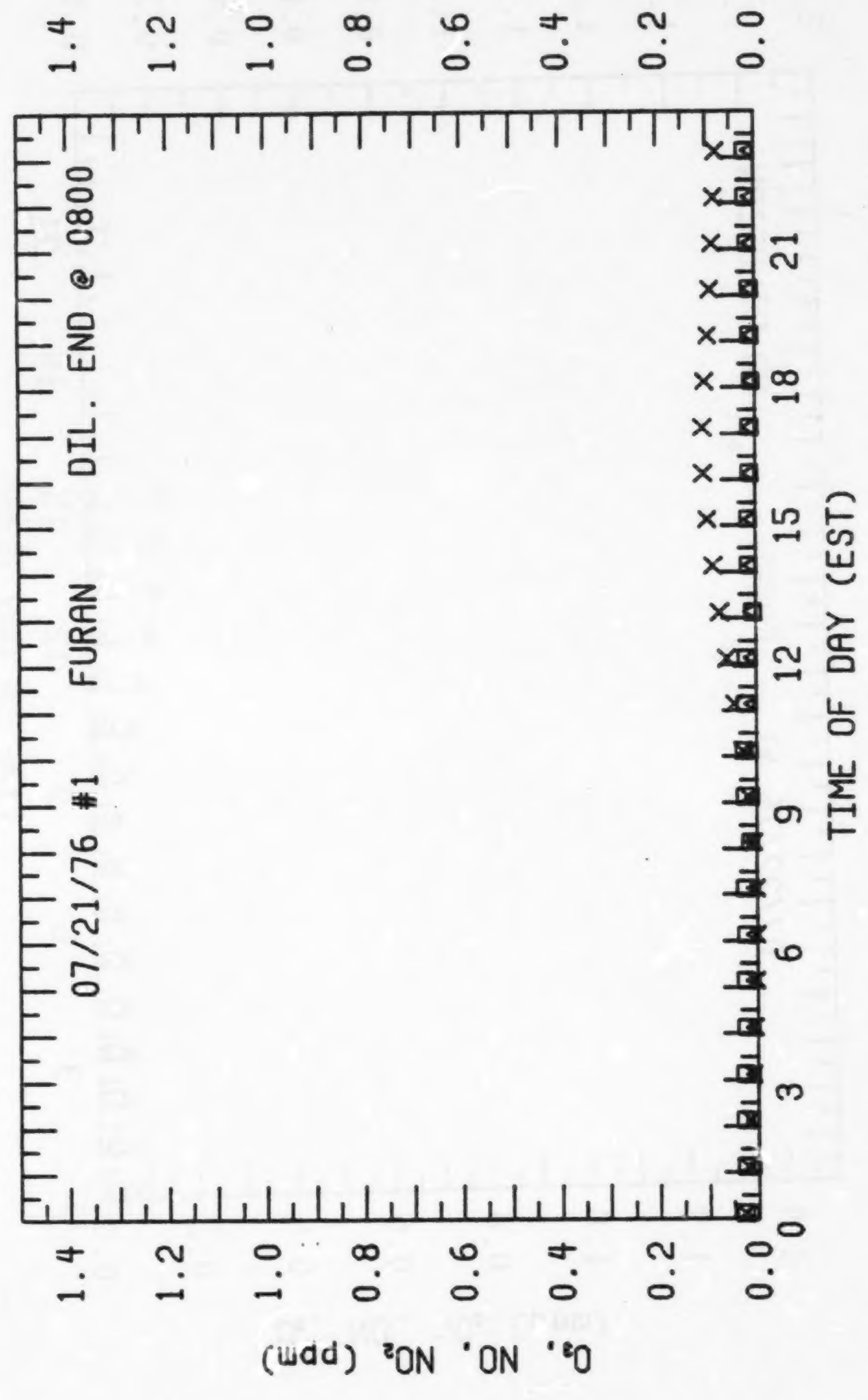
x	Ozone, ppm
□	Nitric Oxide, ppm
Δ	Nitrogen Dioxide, ppm
⌑	Sulfur Dioxide, ppm
*	Solar Radiation (Langleys per minute)

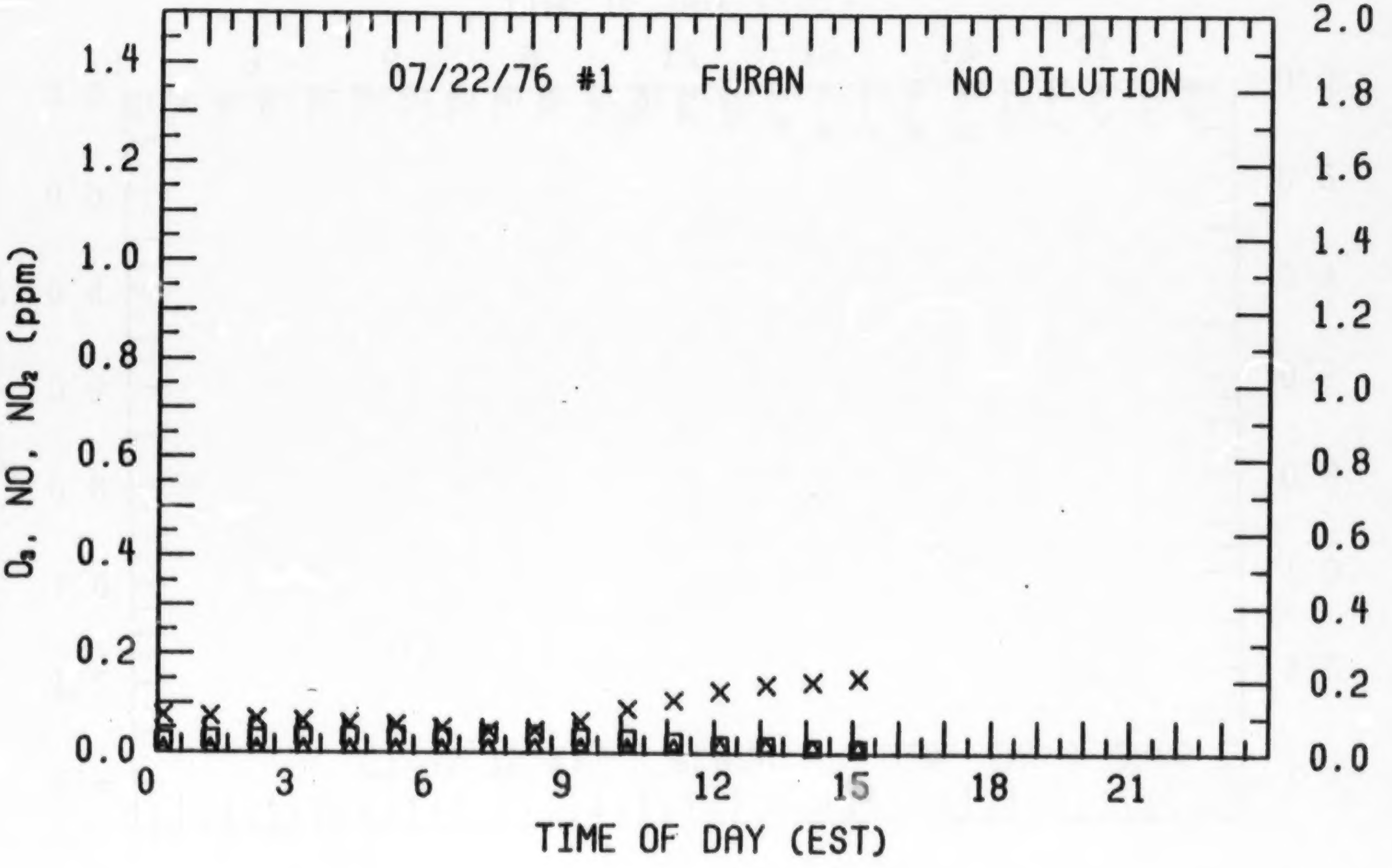

07/20/76
TIME OF DAY (EST)
0
3
6
9
12
15
18
21
SOLAR RAD, LY-MIN^{-1}
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

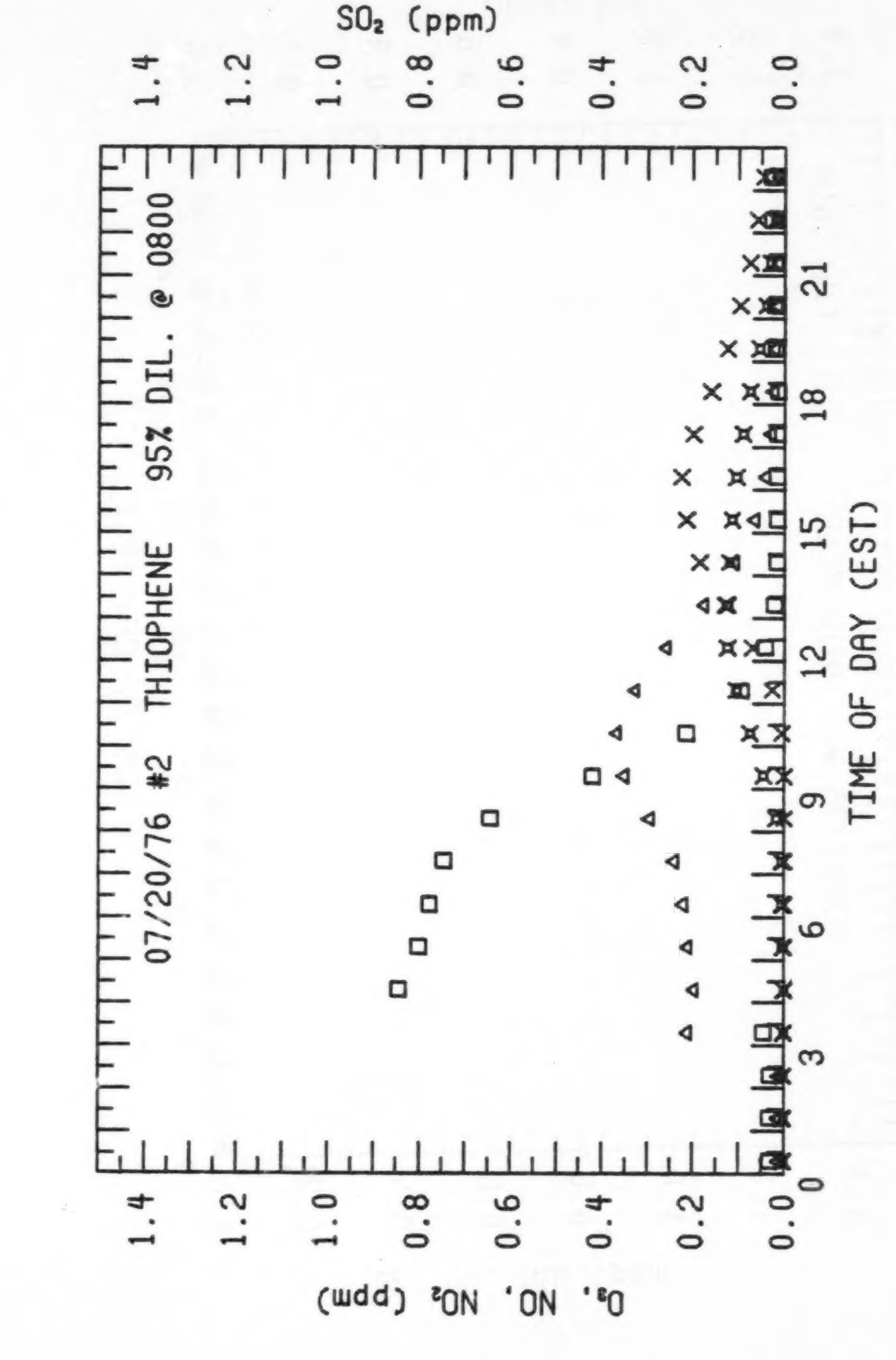

07/21/76
SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

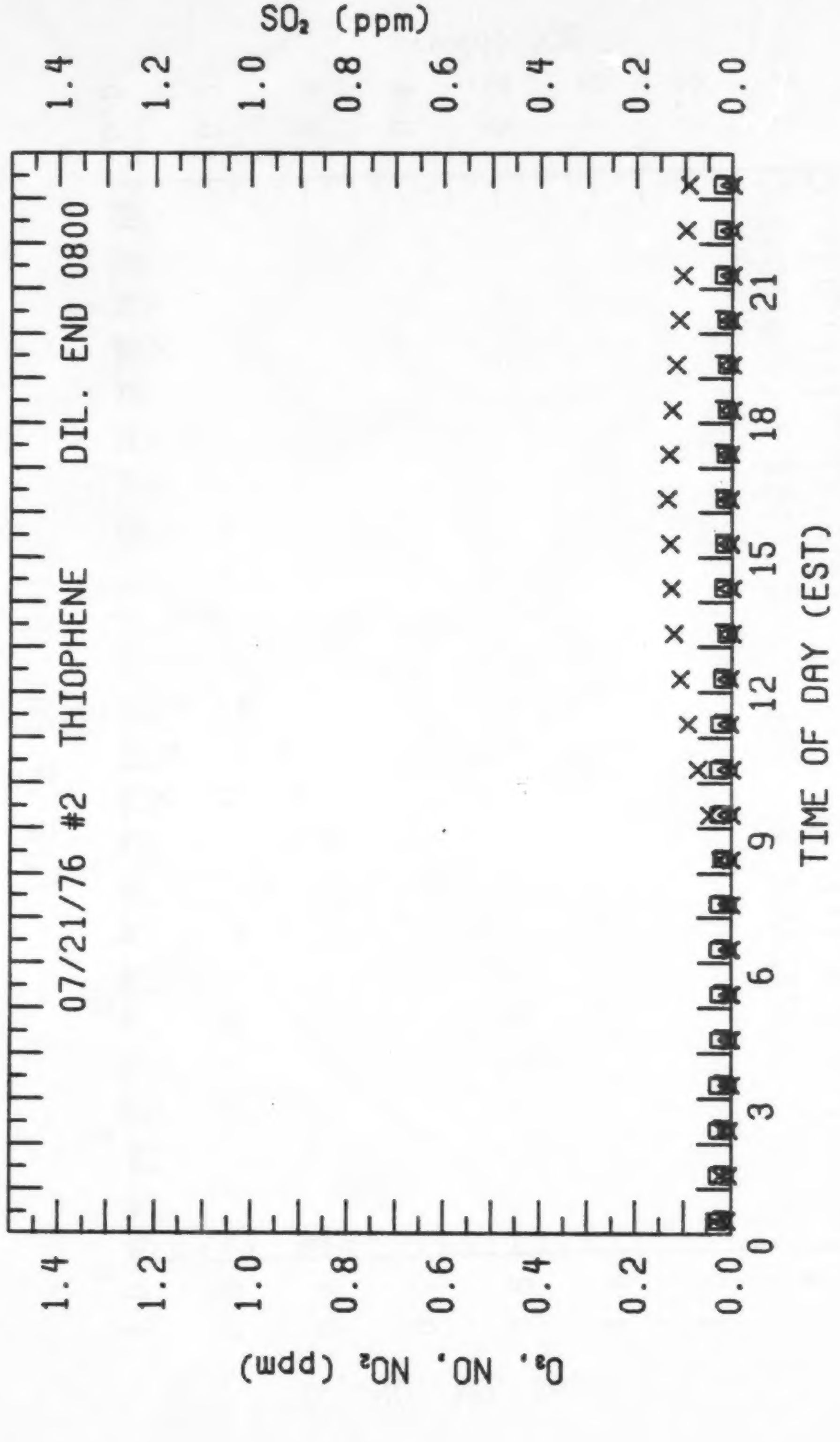

07/22/76
SOLAR RAD, LY-MIN⁻¹
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN⁻¹
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

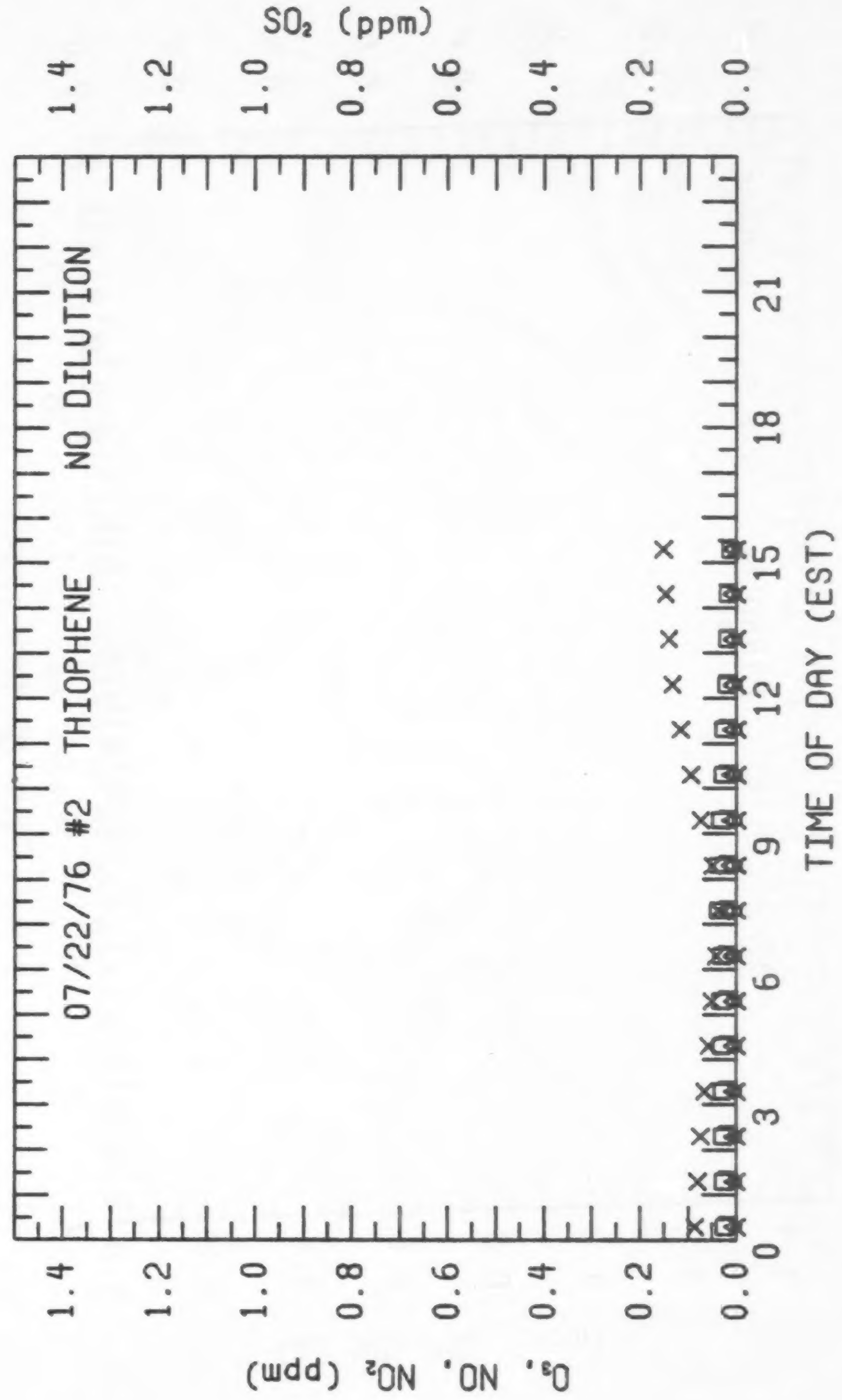

07/20/76 #1 FURAN 95% DIL. @ 0800
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

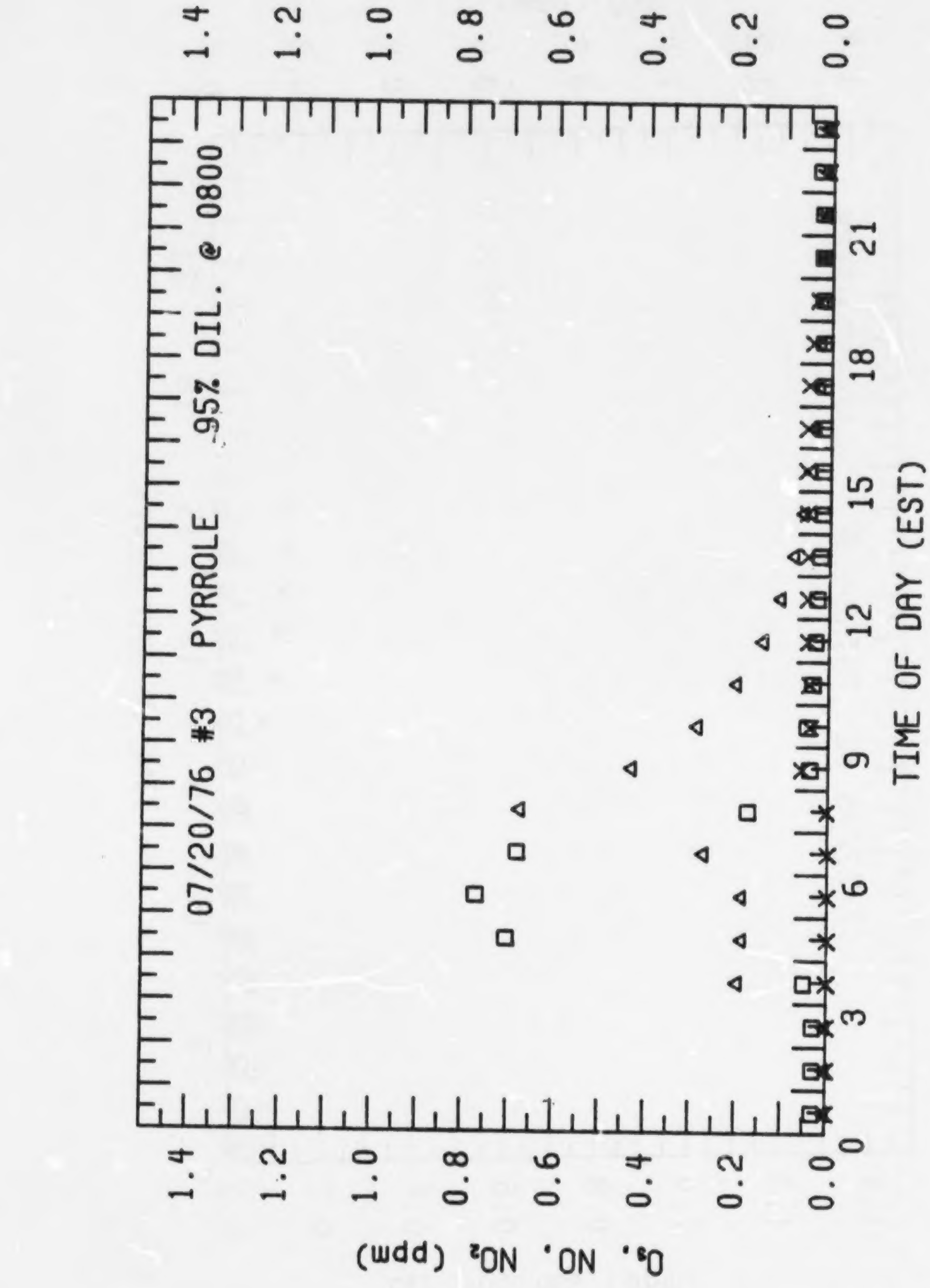

07/21/76 #1 FURAN DIL. END @ 0800
O_3, NO, NO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

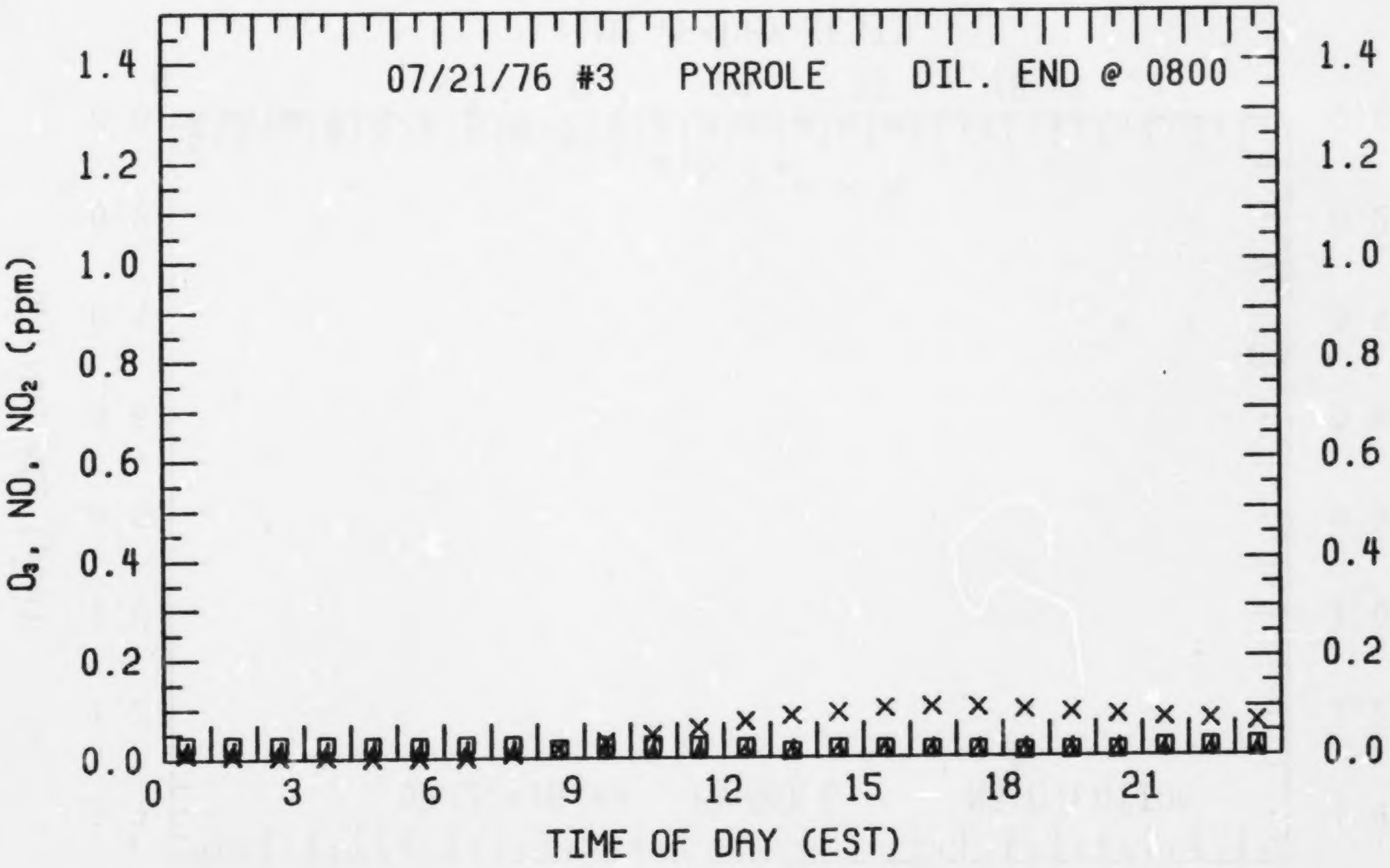

07/22/76 #1
FURAN
NO DILUTION
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

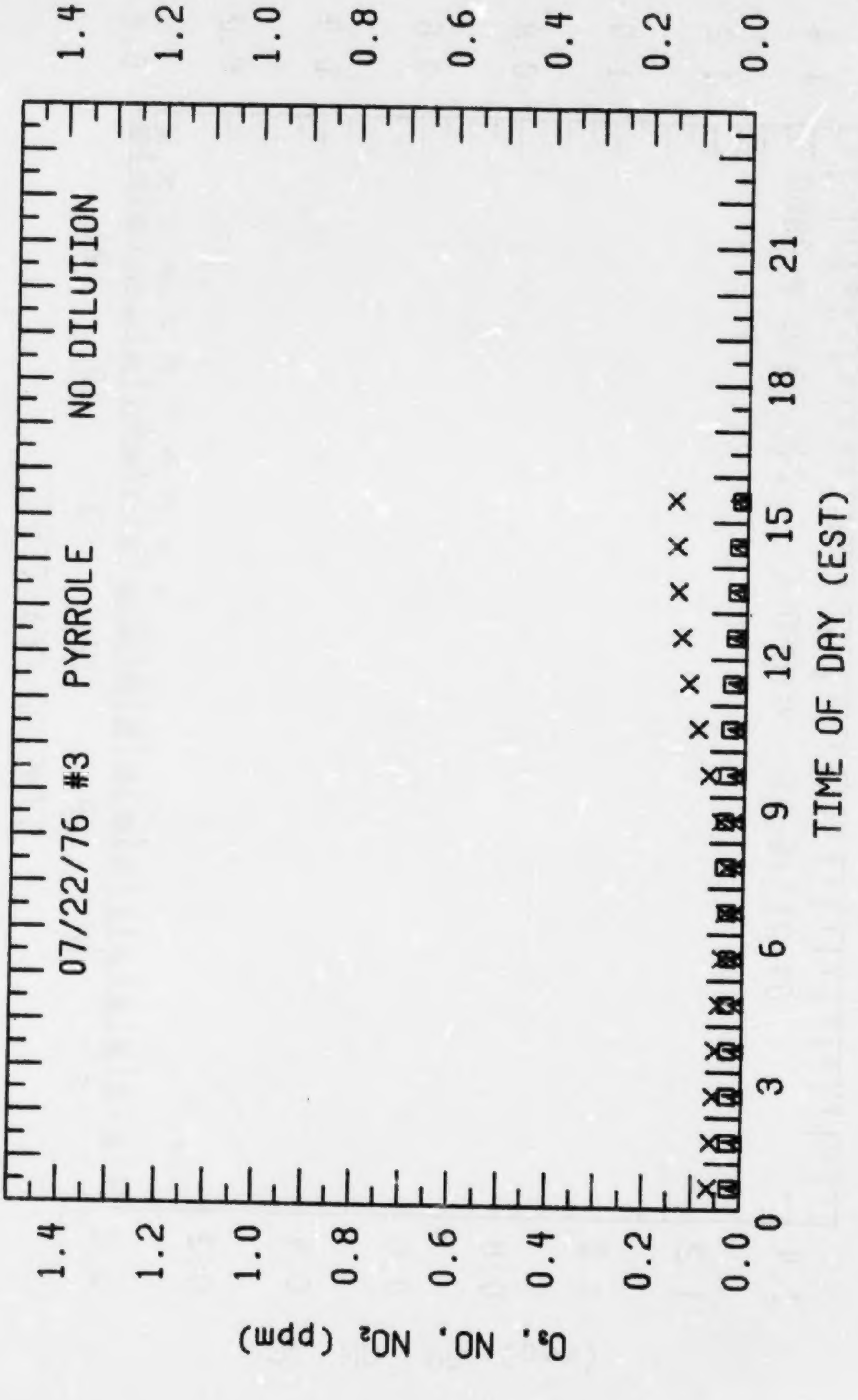

07/20/76 #2 THIOPHENE 95% DIL. @ 0800
SO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

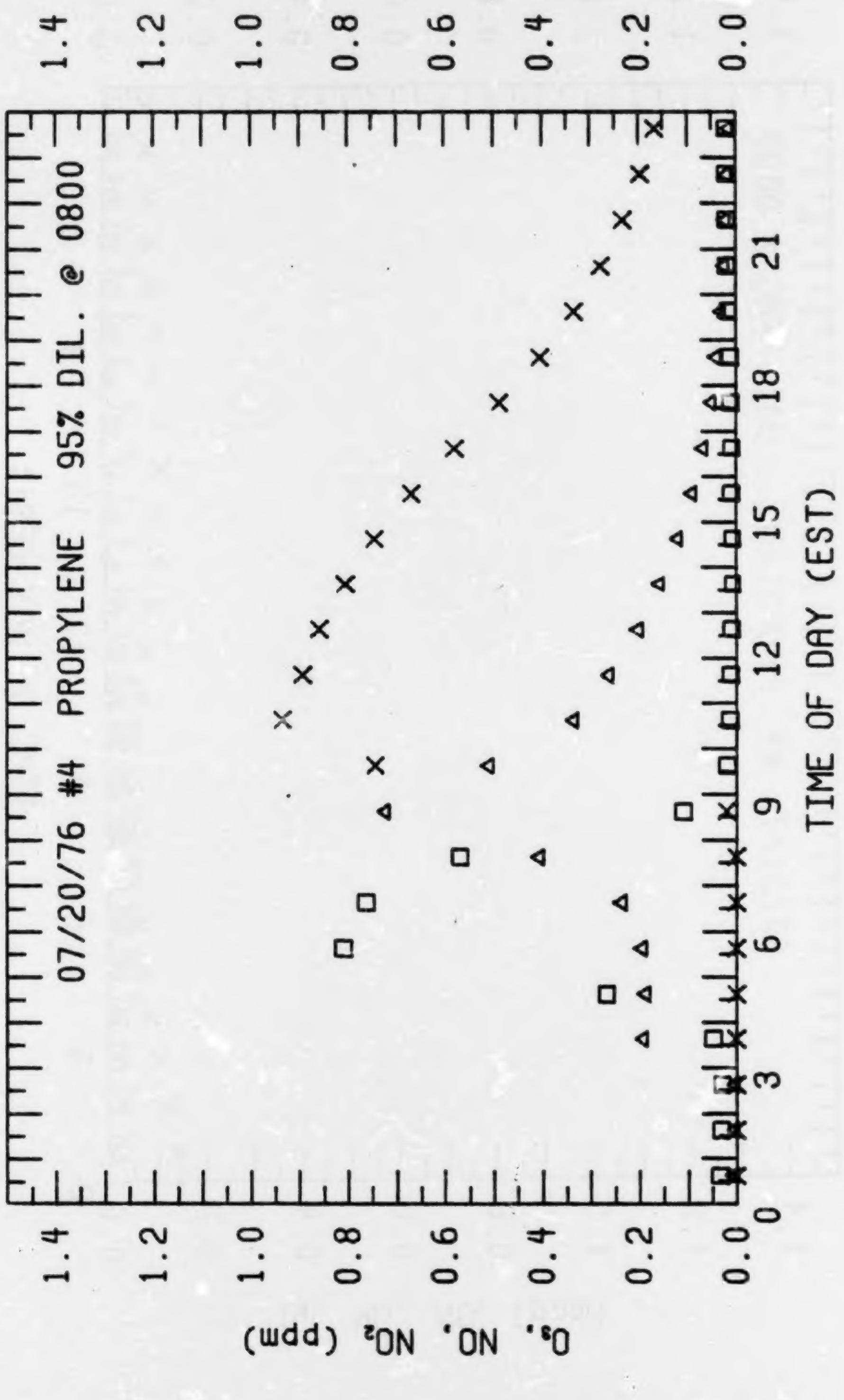

07/21/76 #2 THIOPHENE DIL. END 0800
SO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

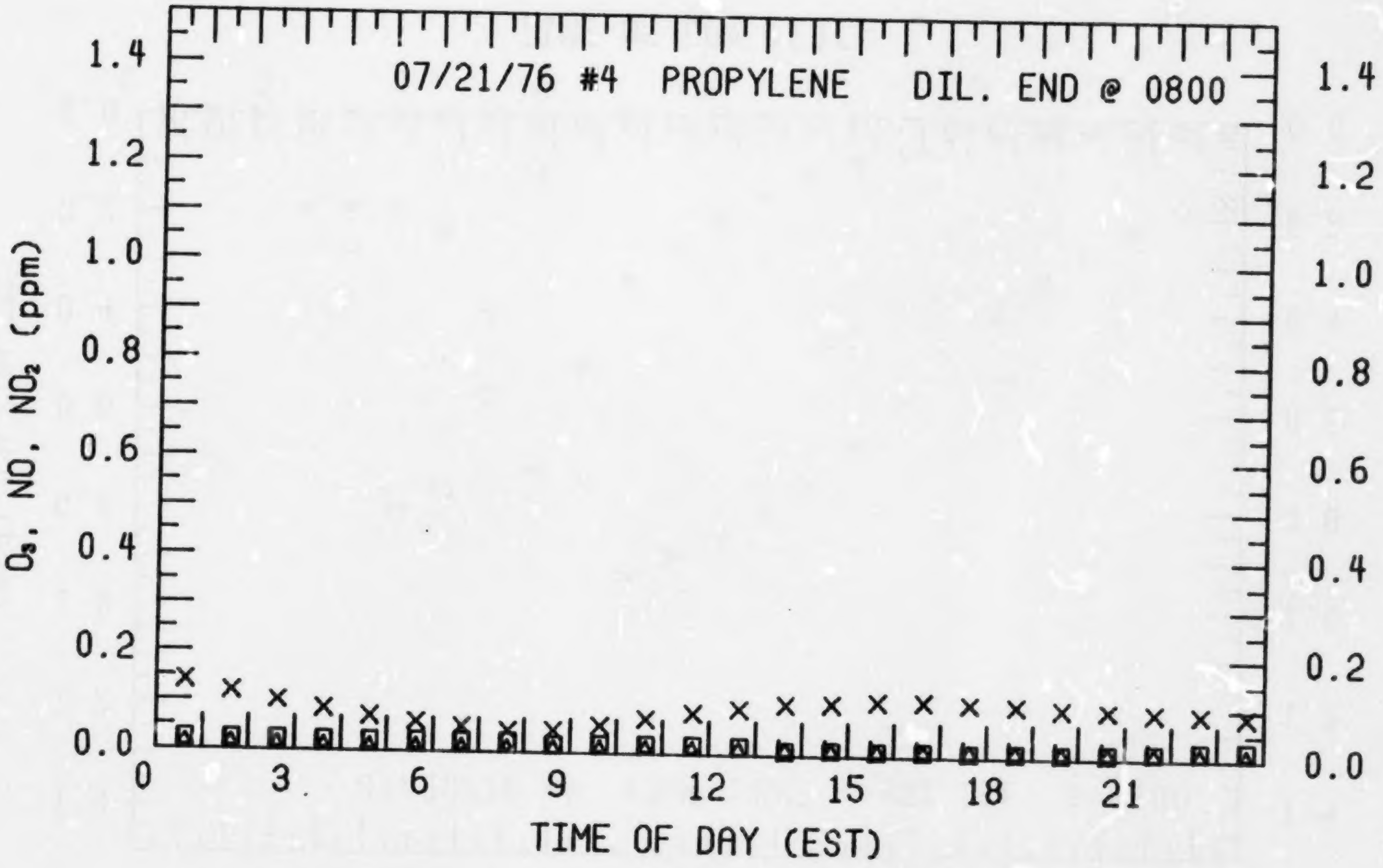

07/22/76 #2 THIOPHENE NO DILUTION
TIME OF DAY (EST)
0
3
6
9
12
15
18
21
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

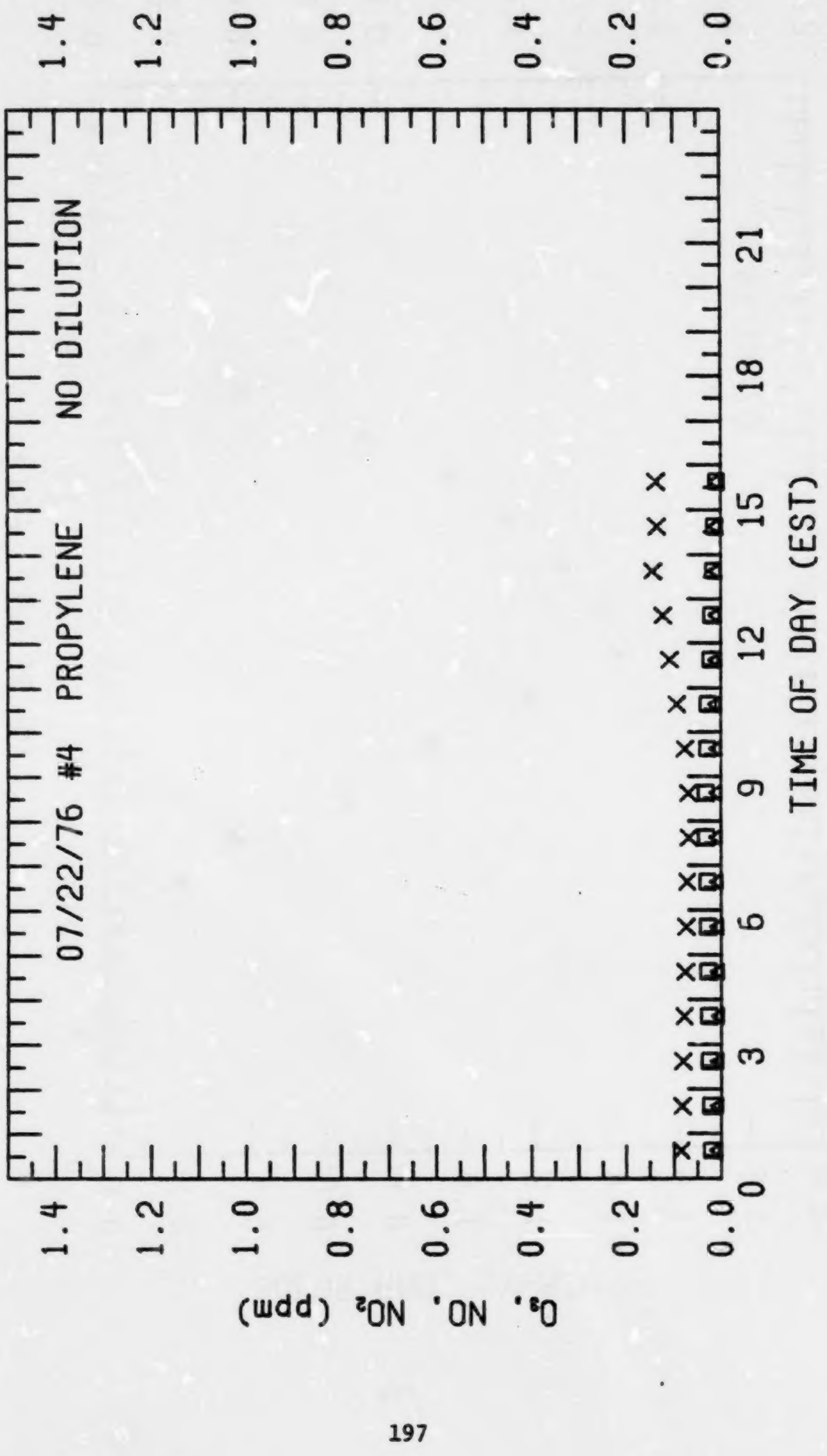

07/20/76 #3 PYRROLE 95% DIL. @ 0800
O3, NO, NO2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

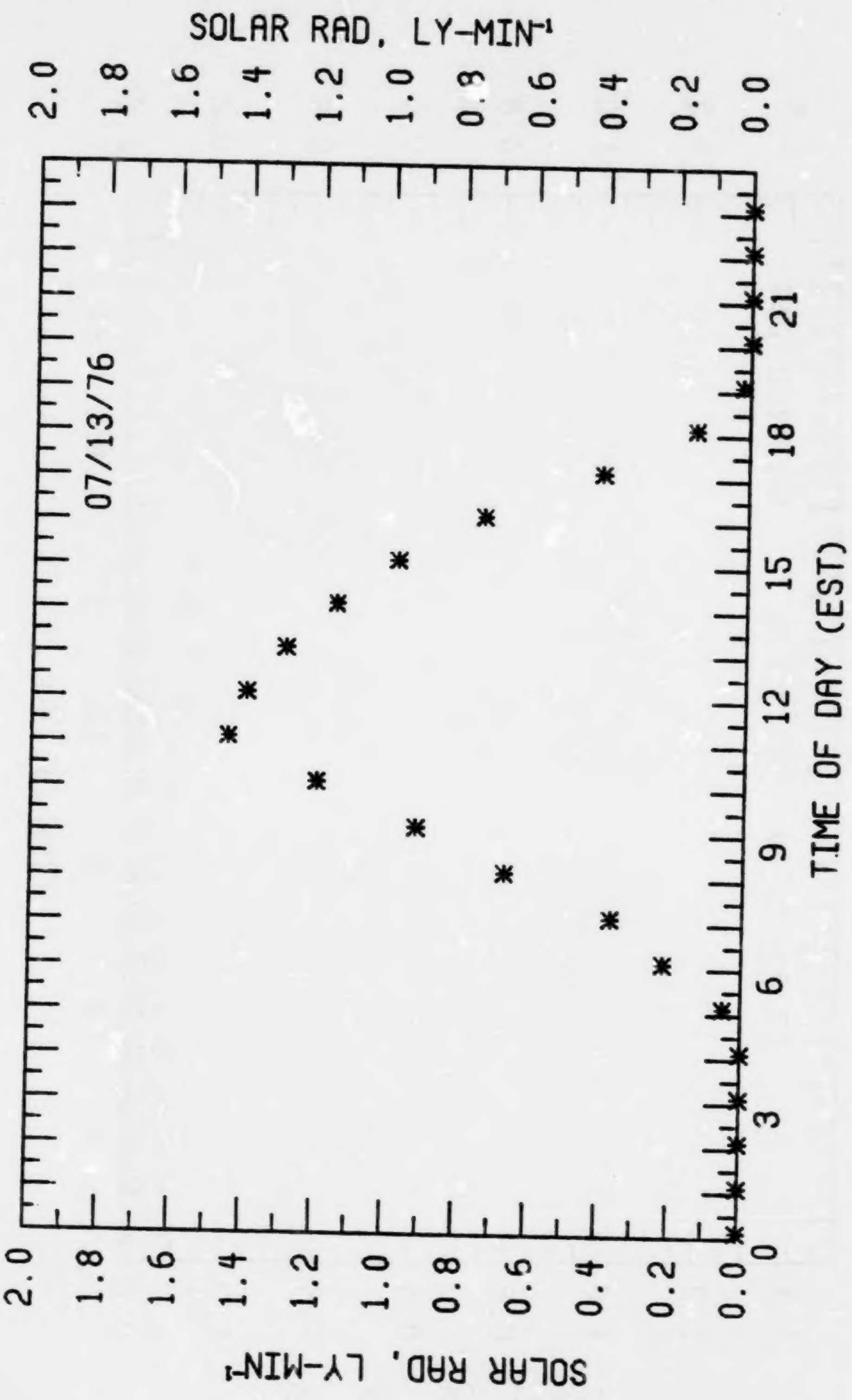

07/21/76 #3 PYRROLE DIL. END @ 0800
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

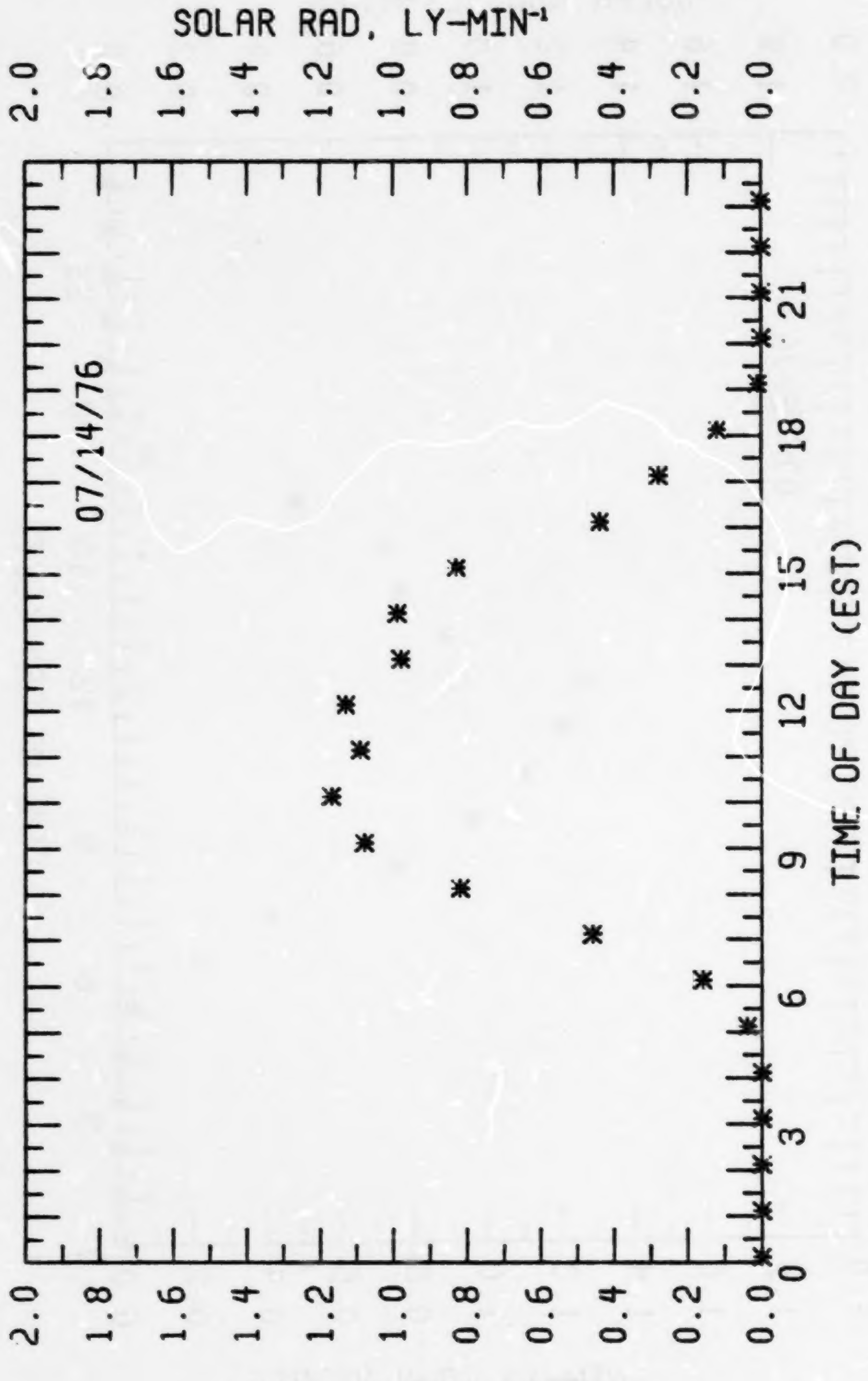

07/22/76 #3 PYRROLE NO DILUTION
O$_3$, NO, NO$_2$ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

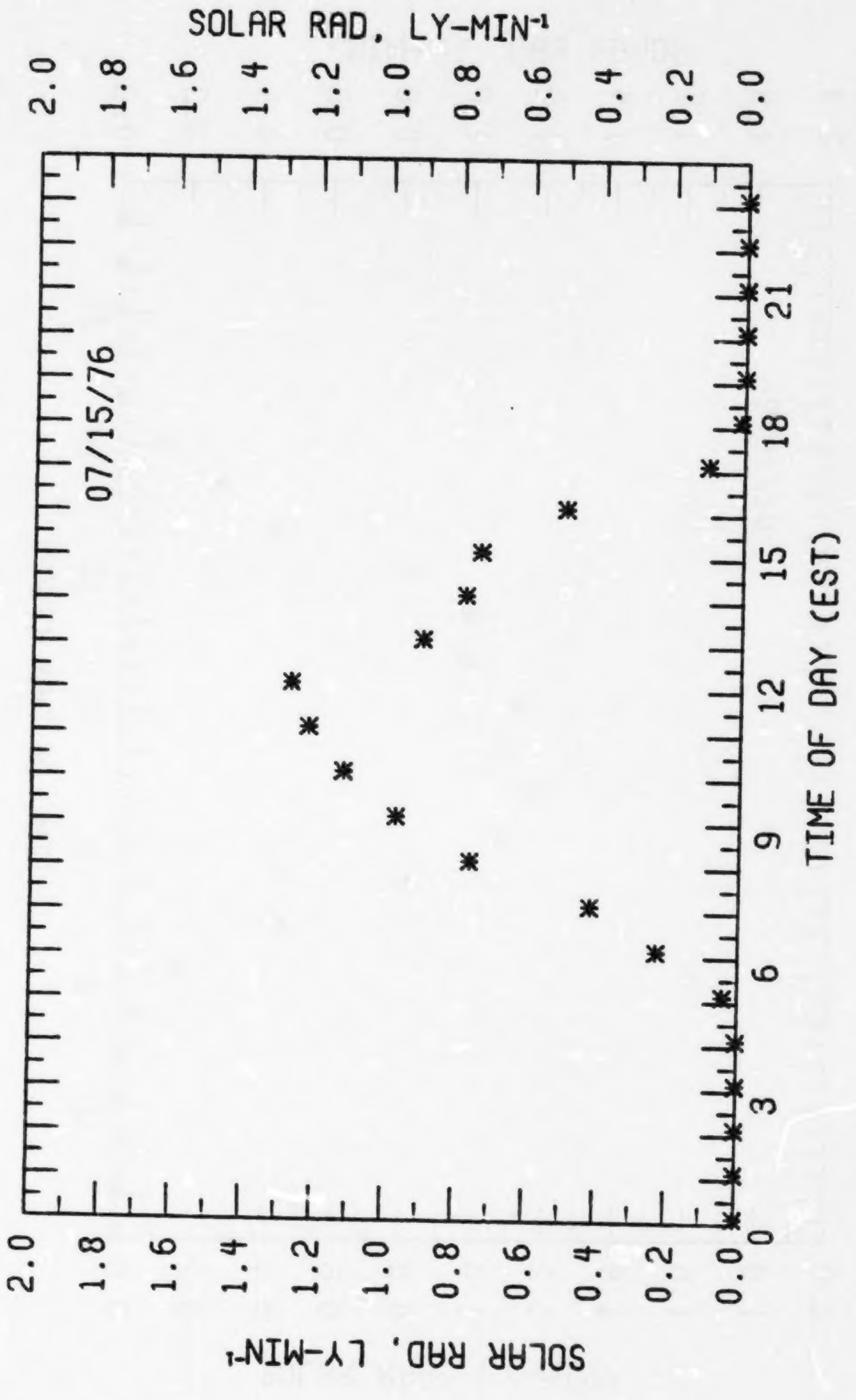

07/20/76 #4 PROPYLENE 95% DIL. @ 0800
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

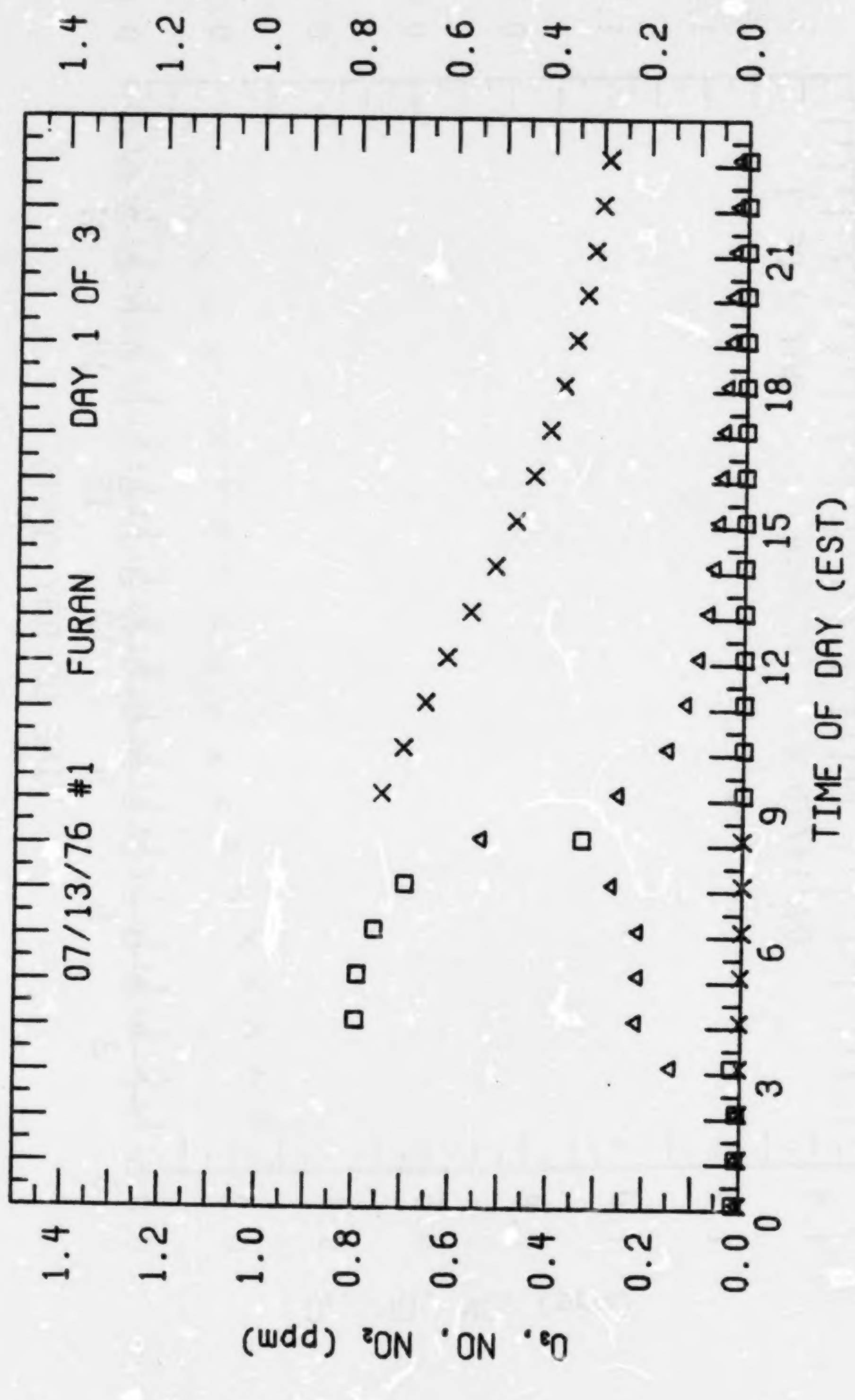

07/21/76 #4 PROPYLENE DIL. END @ 0800
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

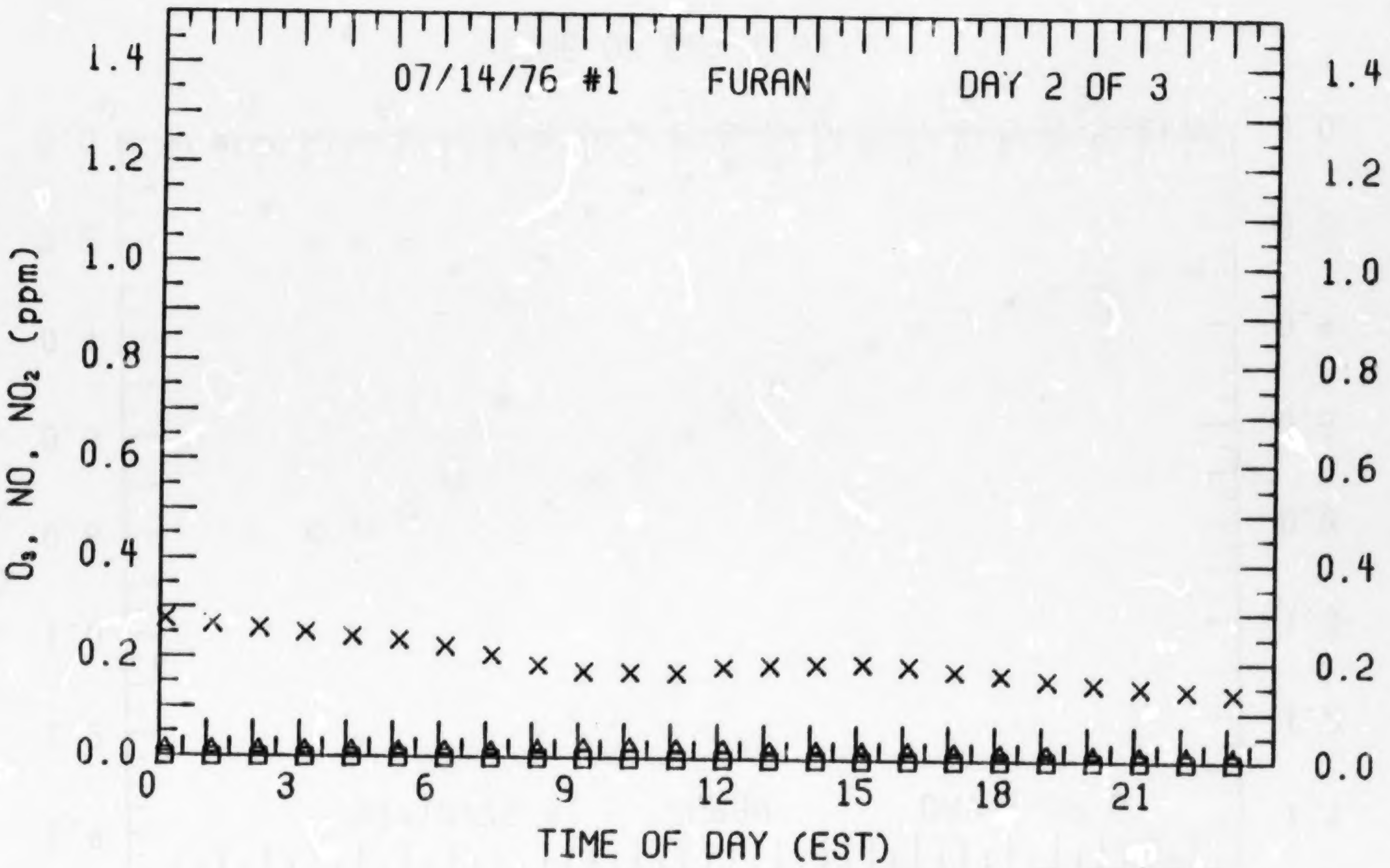

07/22/76 #4 PROPYLENE NO DILUTION
O_3, NO, NO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

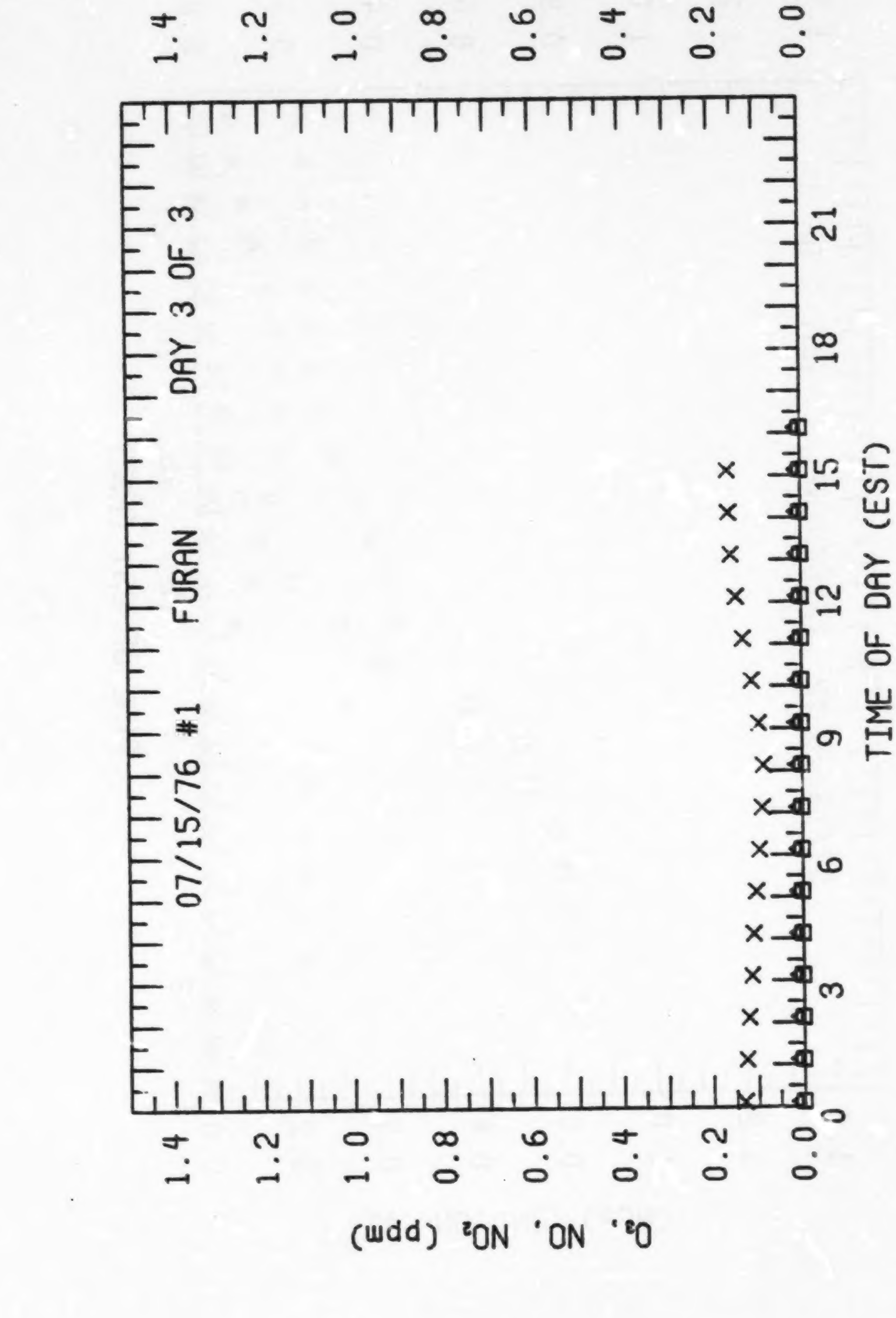

07/13/76
SOLAR RAD, LY-MIN-1
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

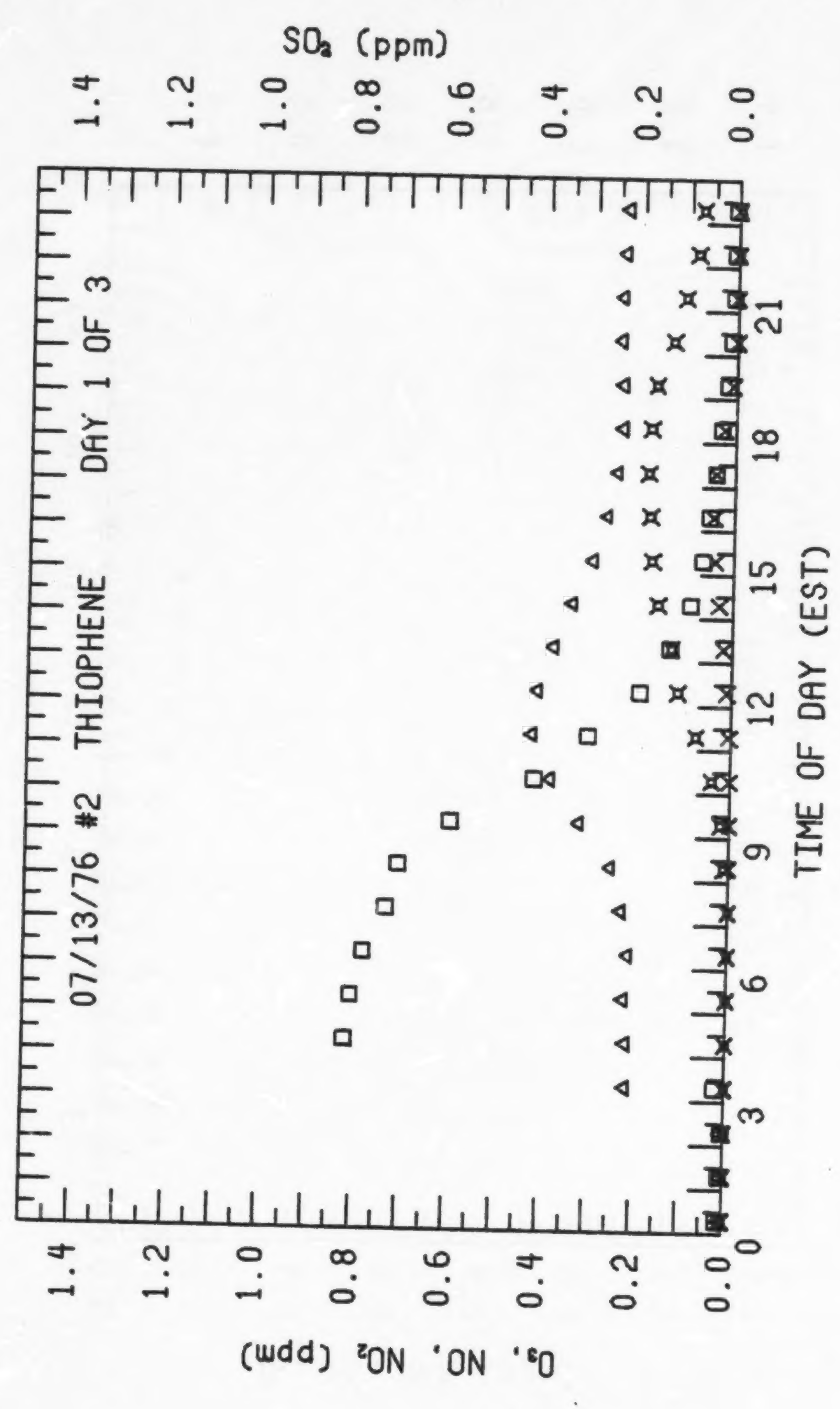
SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
07/14/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

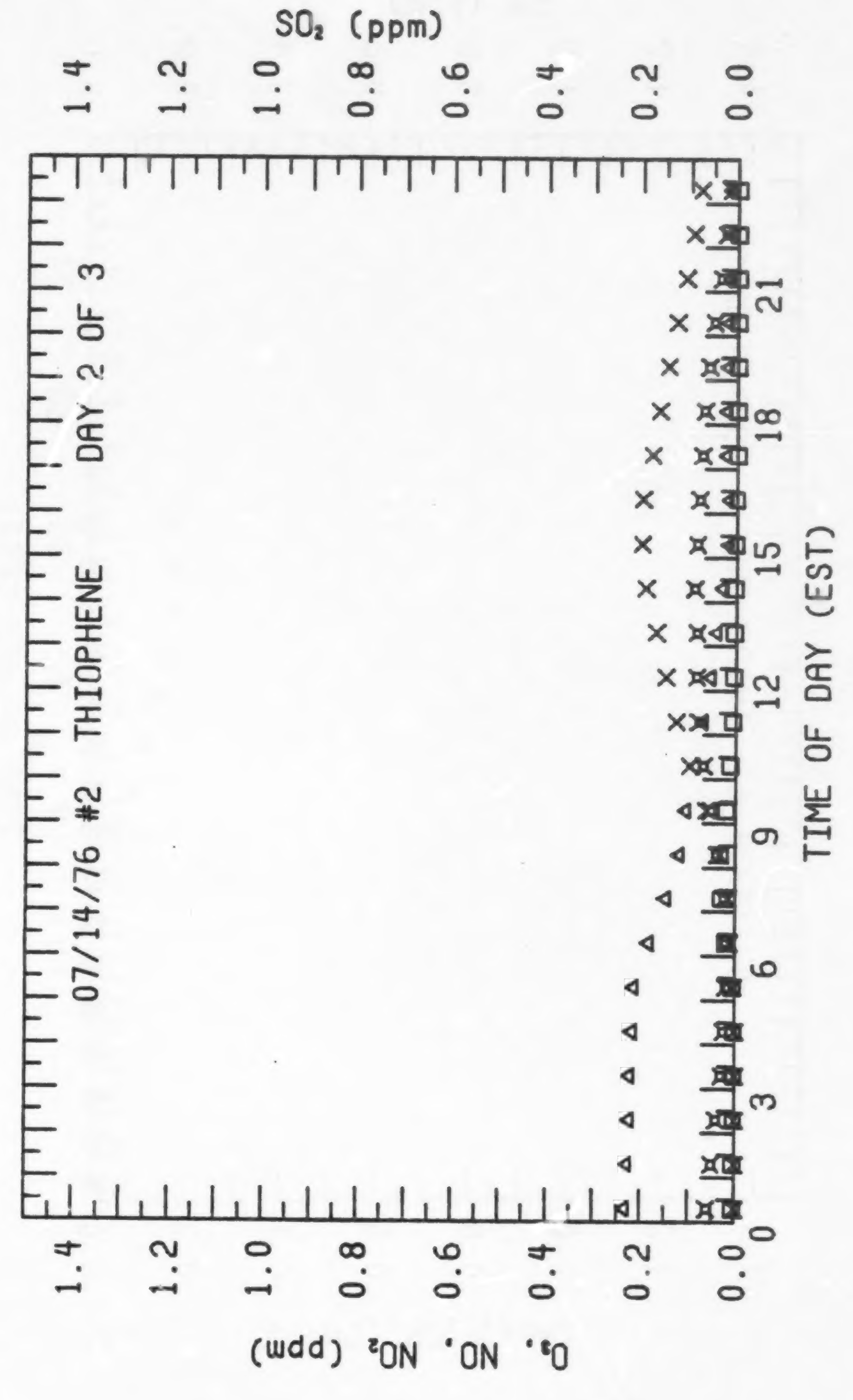

SOLAR RAD, LY-MIN⁻¹
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
07/15/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN⁻¹

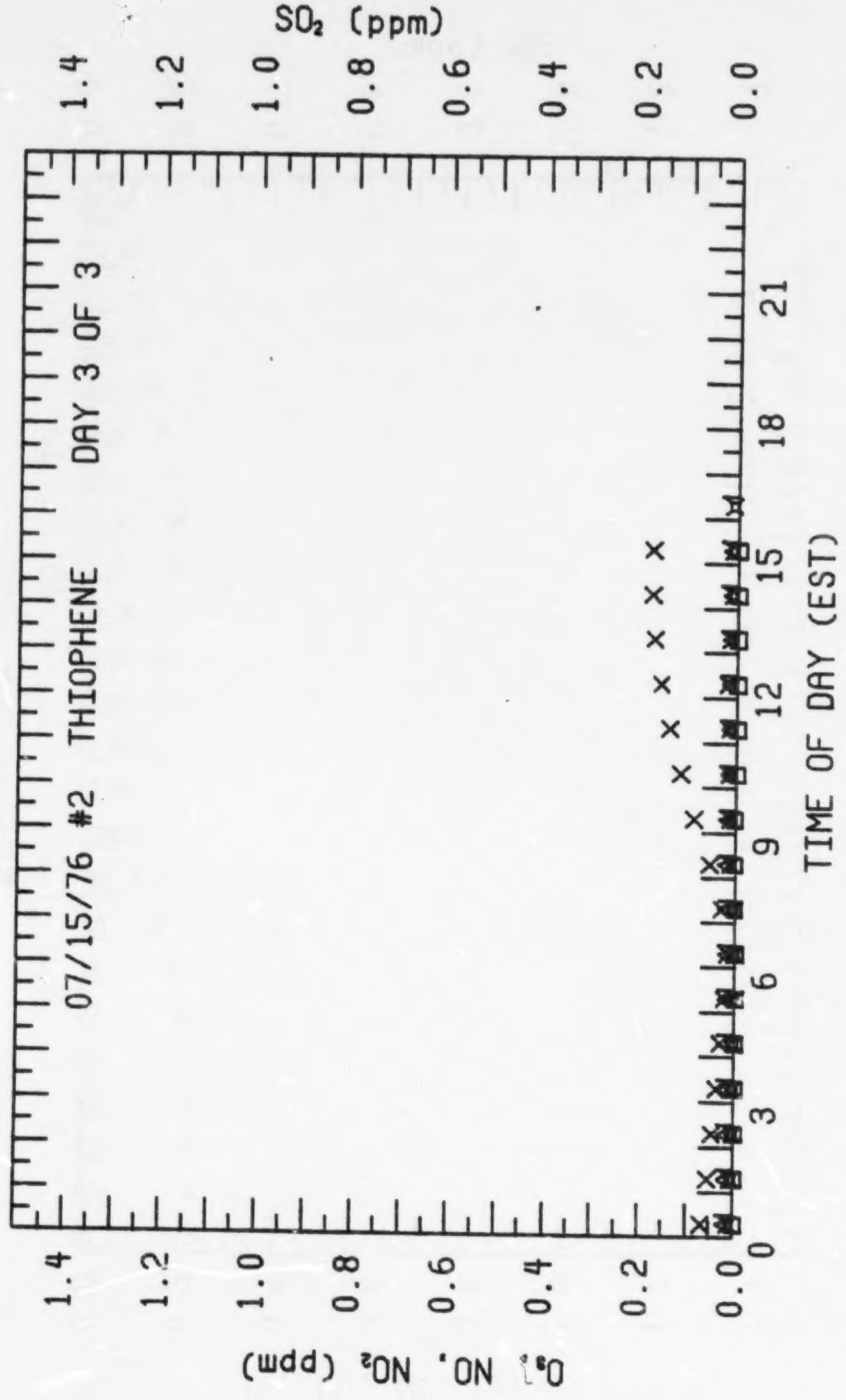

07/13/76 #1
FURAN
DAY 1 OF 3
O_3, NO, NO_2 (ppm)
TIME OF DAY (EST)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
3
6
9
12
15
18
21

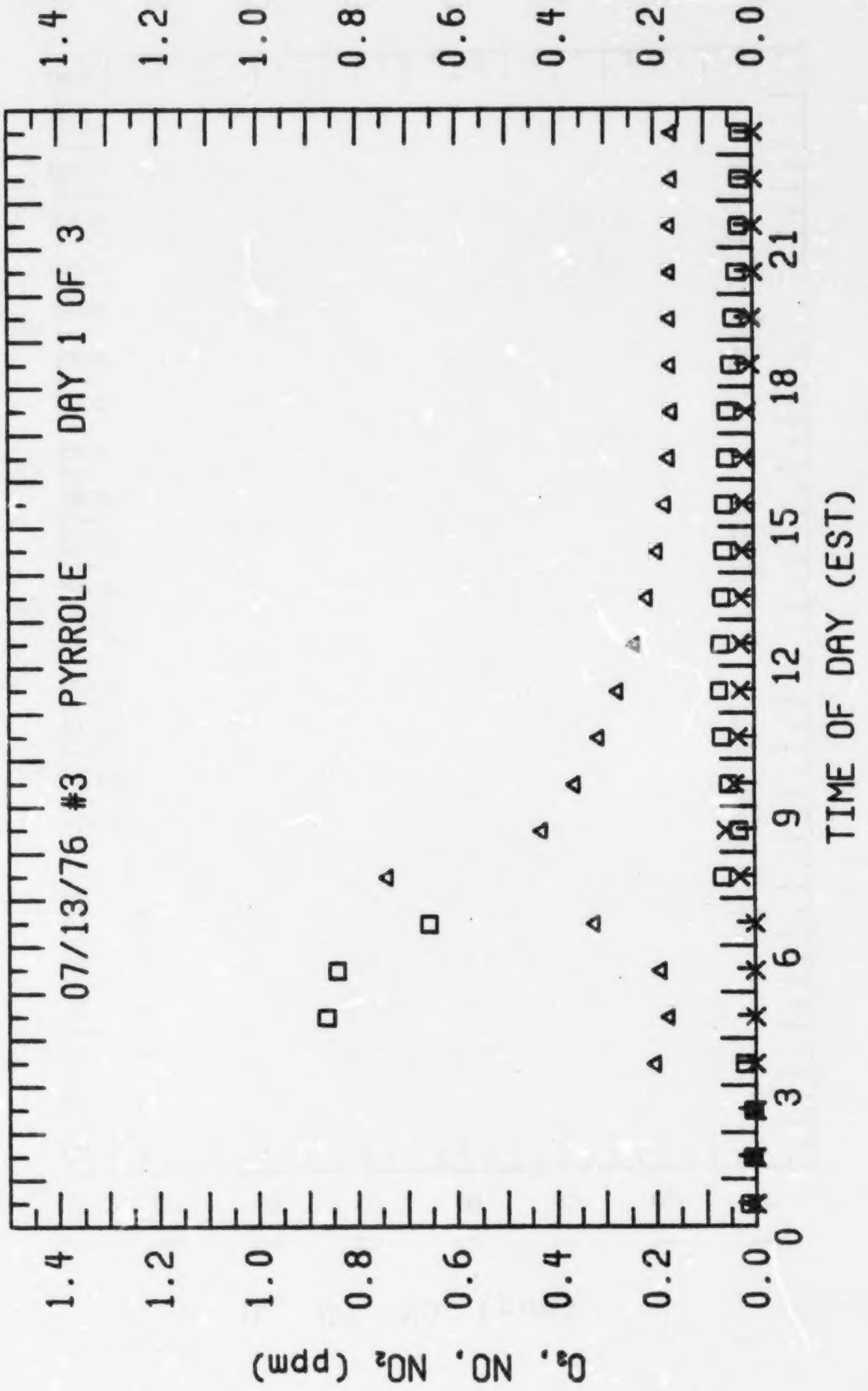

07/14/76 #1 FURAN DAY 2 OF 3
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)


07/15/76 #1
FURAN
DAY 3 OF 3
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

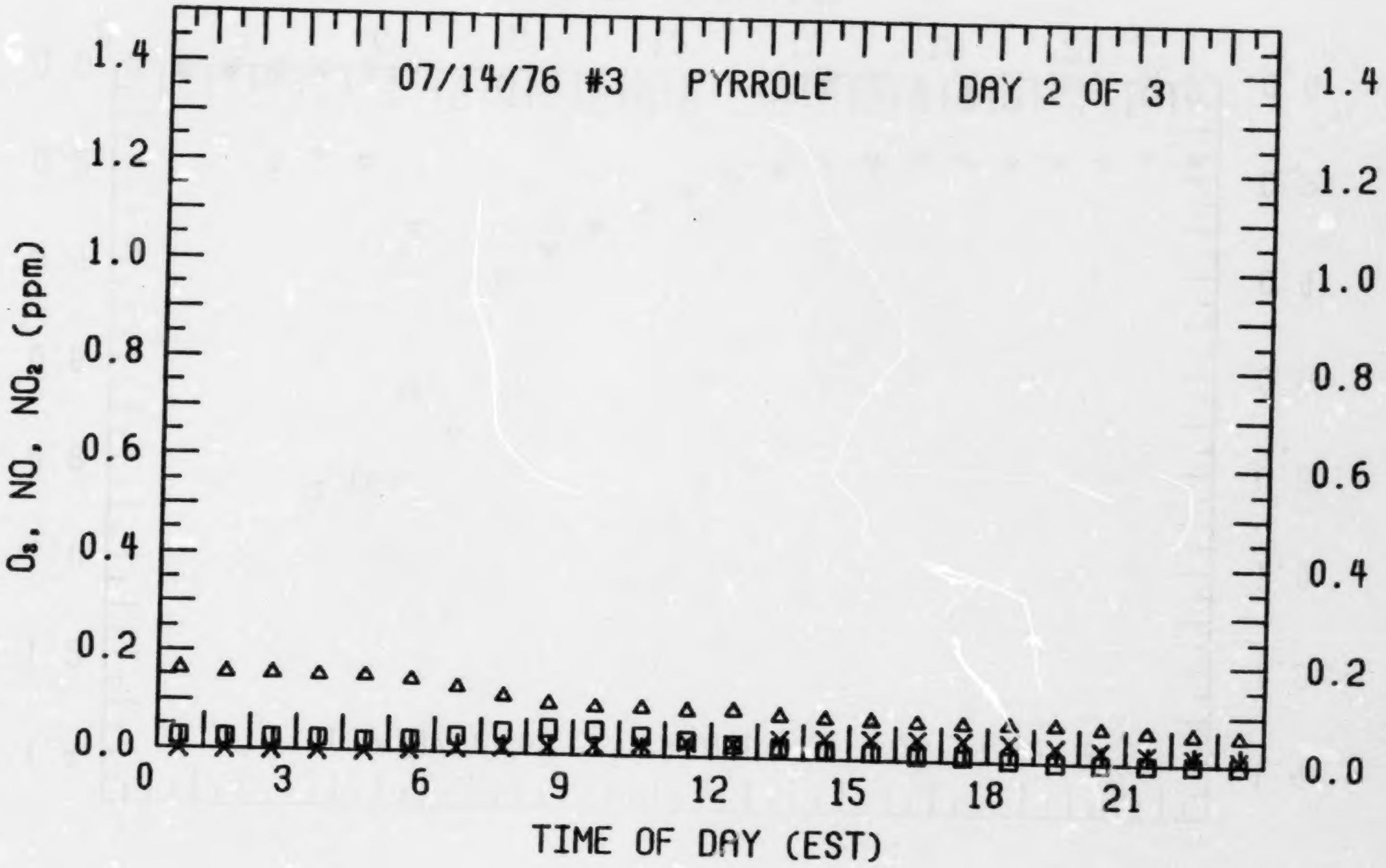

07/13/76 #2 THIOPHENE DAY 1 OF 3
TIME OF DAY (EST)
0
3
6
9
12
15
18
21
O_3, NO, NO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

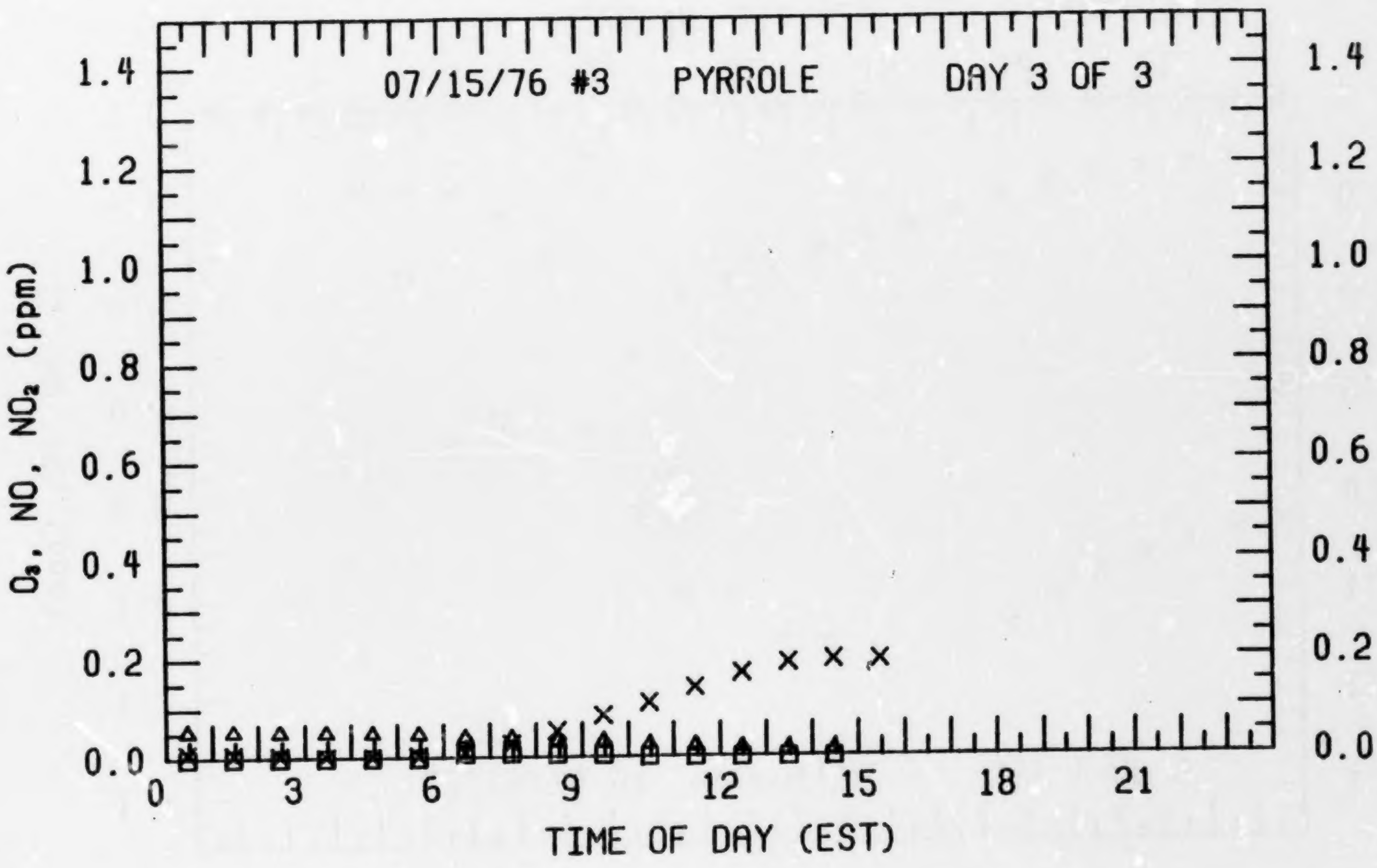

07/14/76 #2 THIOPHENE DAY 2 OF 3
O_3, NO, NO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

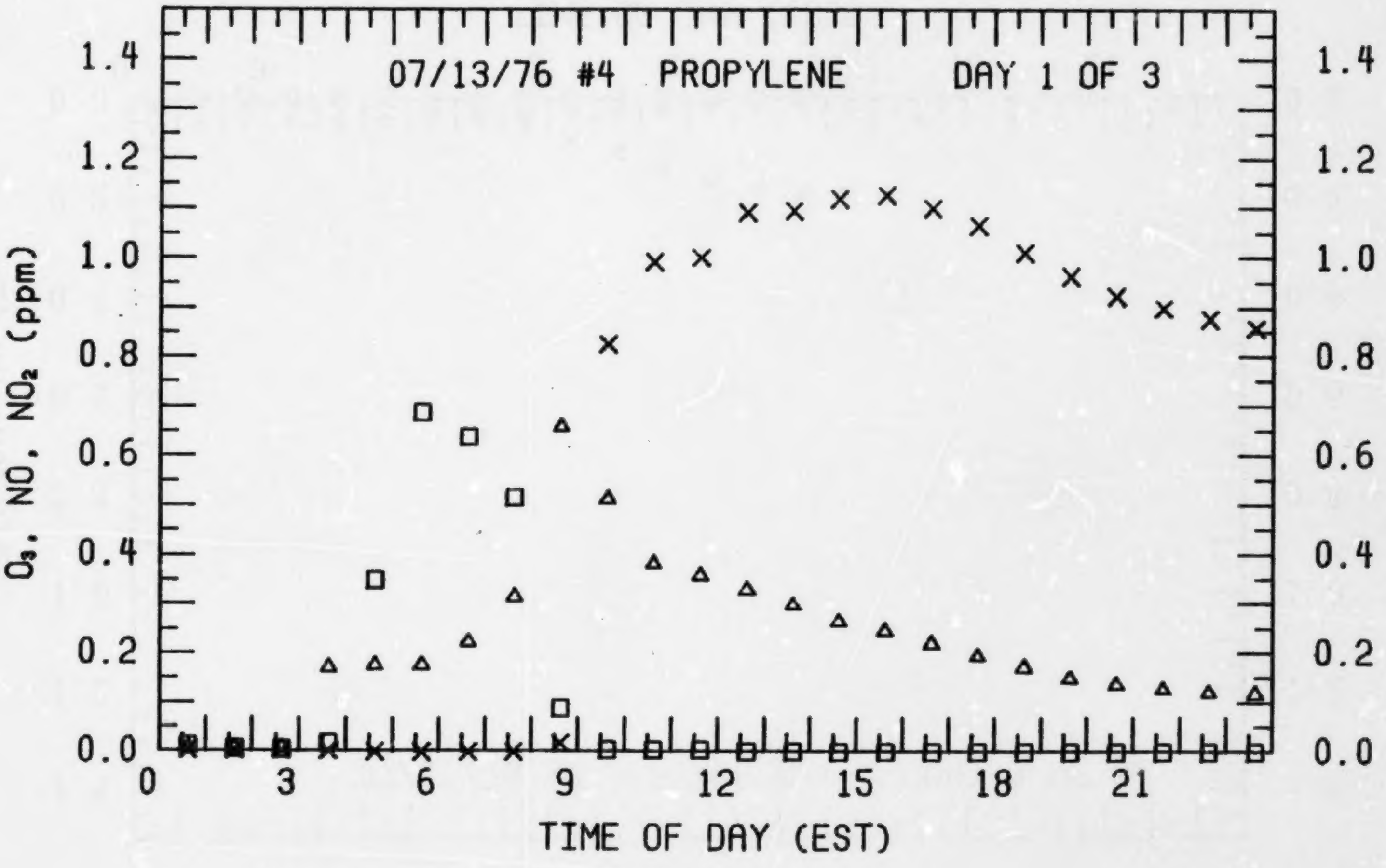

07/15/76 #2 THIOPHENE DAY 3 OF 3
TIME OF DAY (EST)
0
3
6
9
12
15
18
21
O_3, NO, NO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

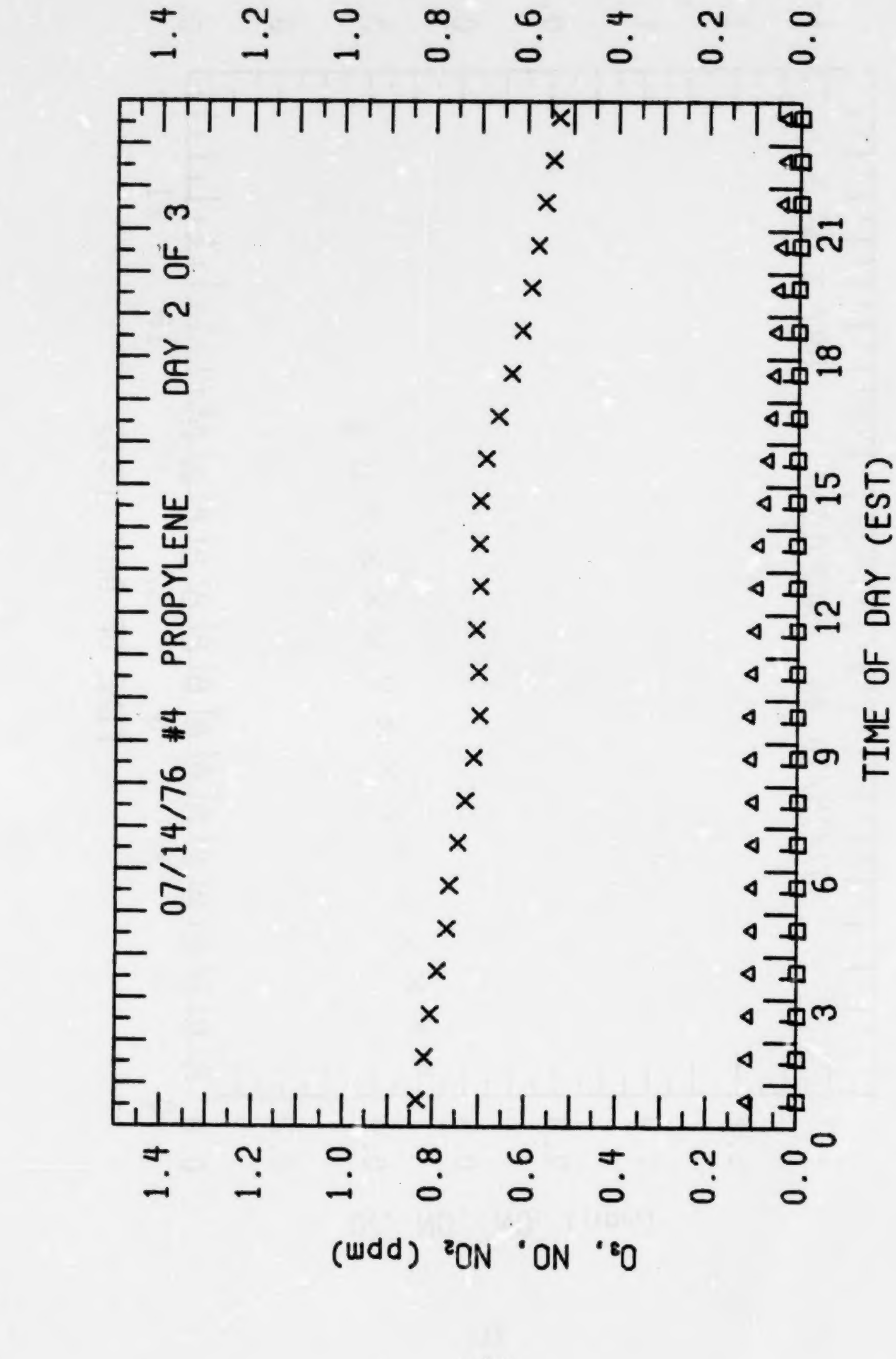


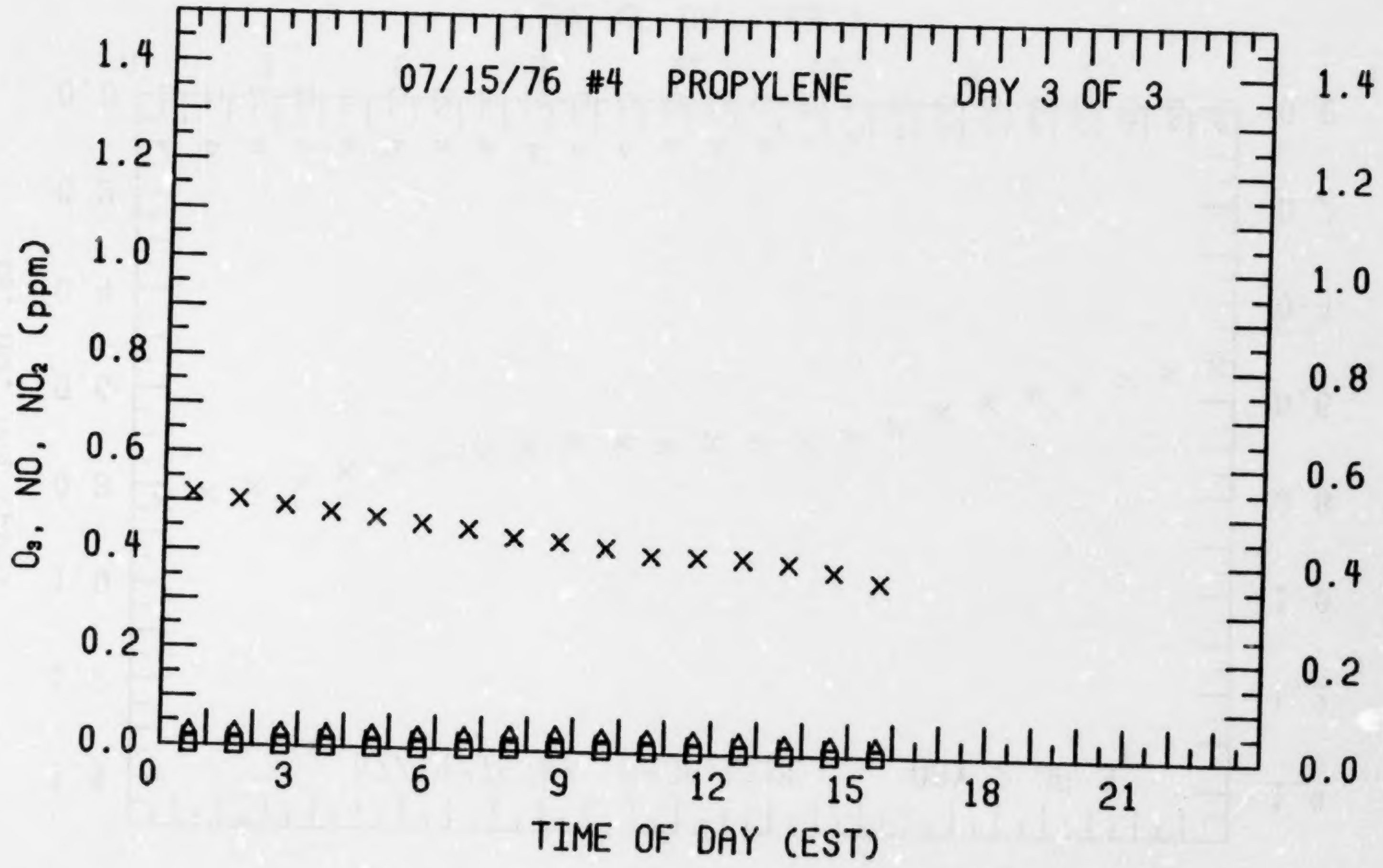
07/13/76 #3 PYRROLE DAY 1 OF 3
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

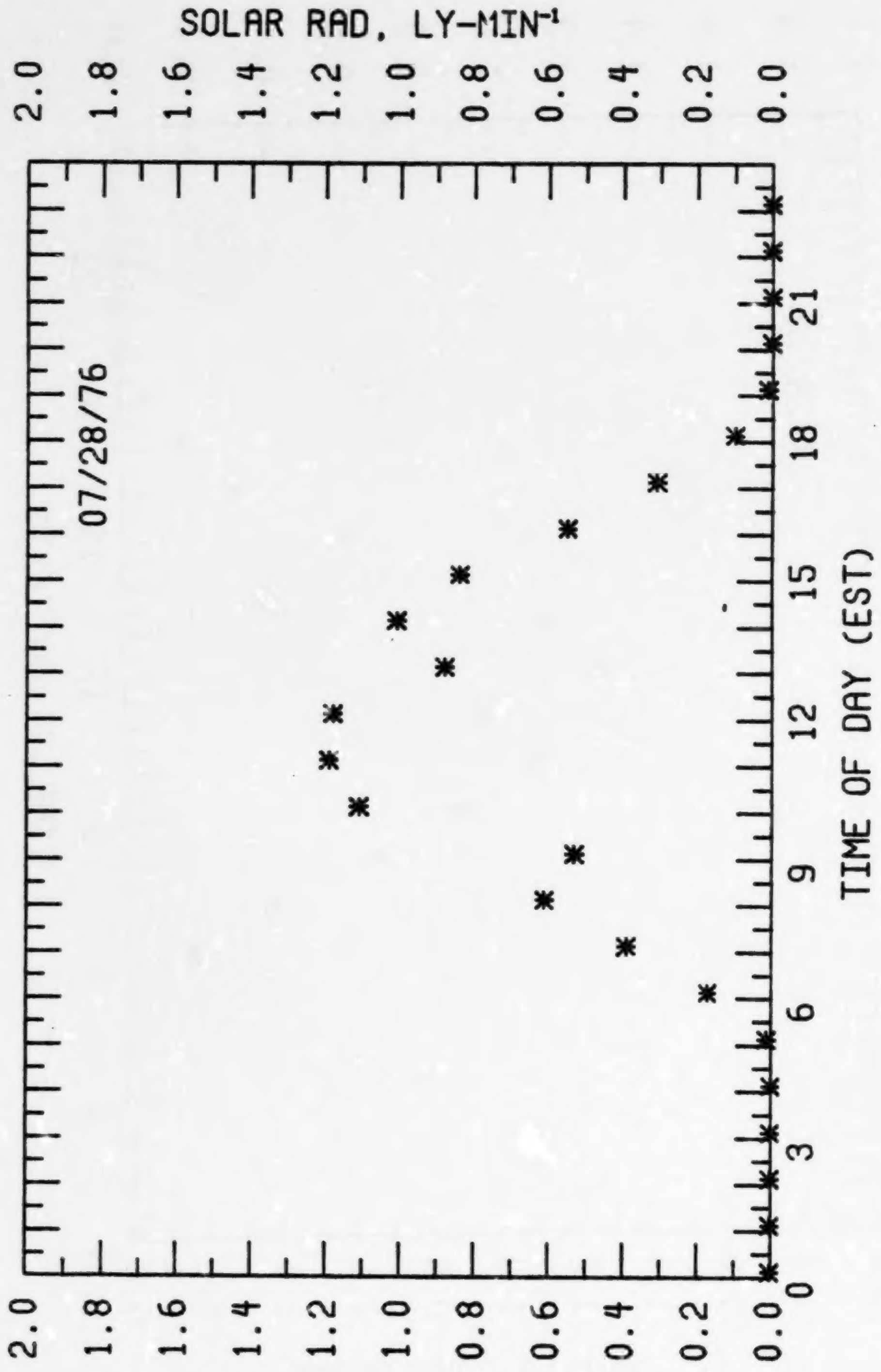

07/14/76 #3 PYRROLE DAY 2 OF 3
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

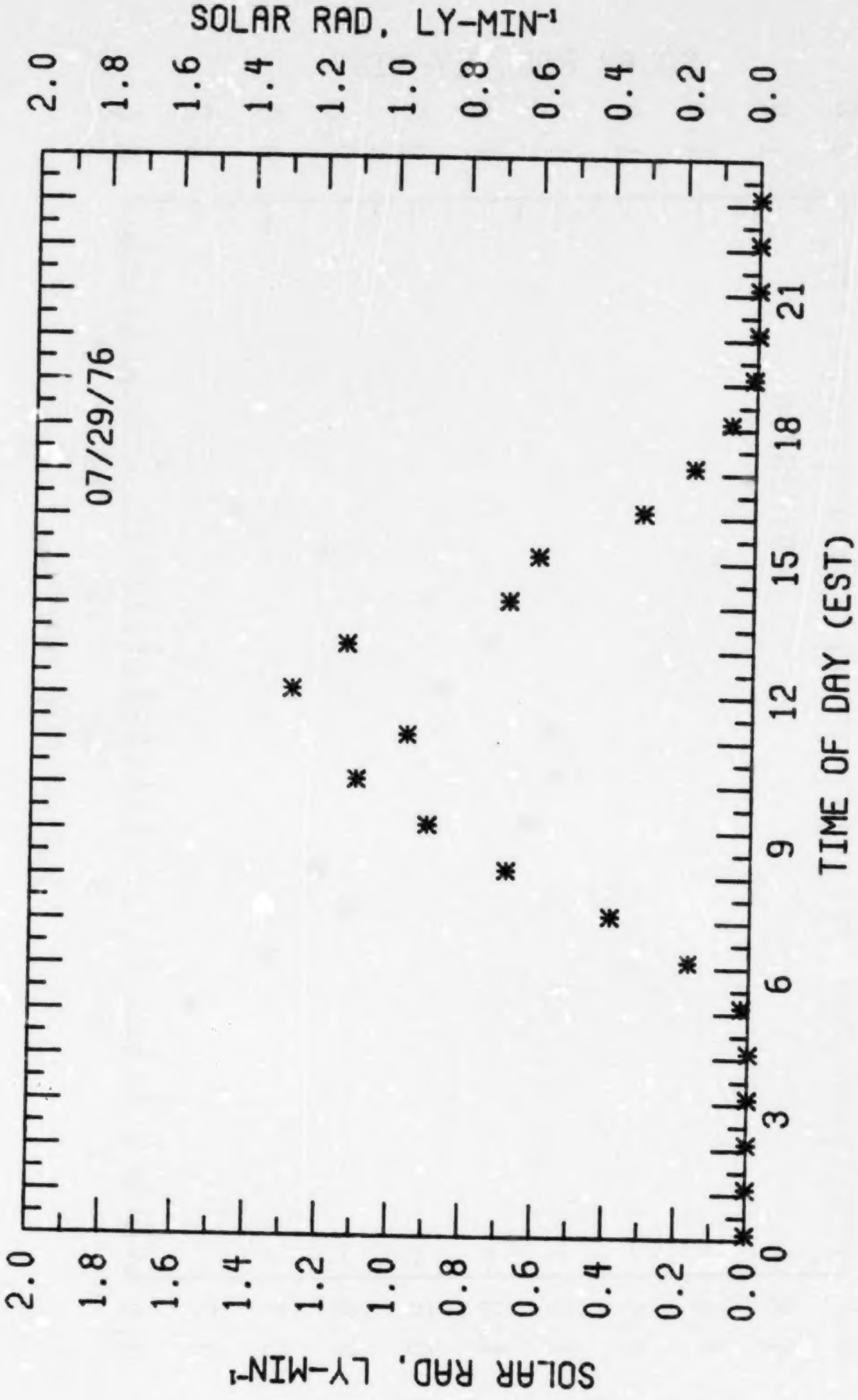

07/15/76 #3 PYRROLE DAY 3 OF 3
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

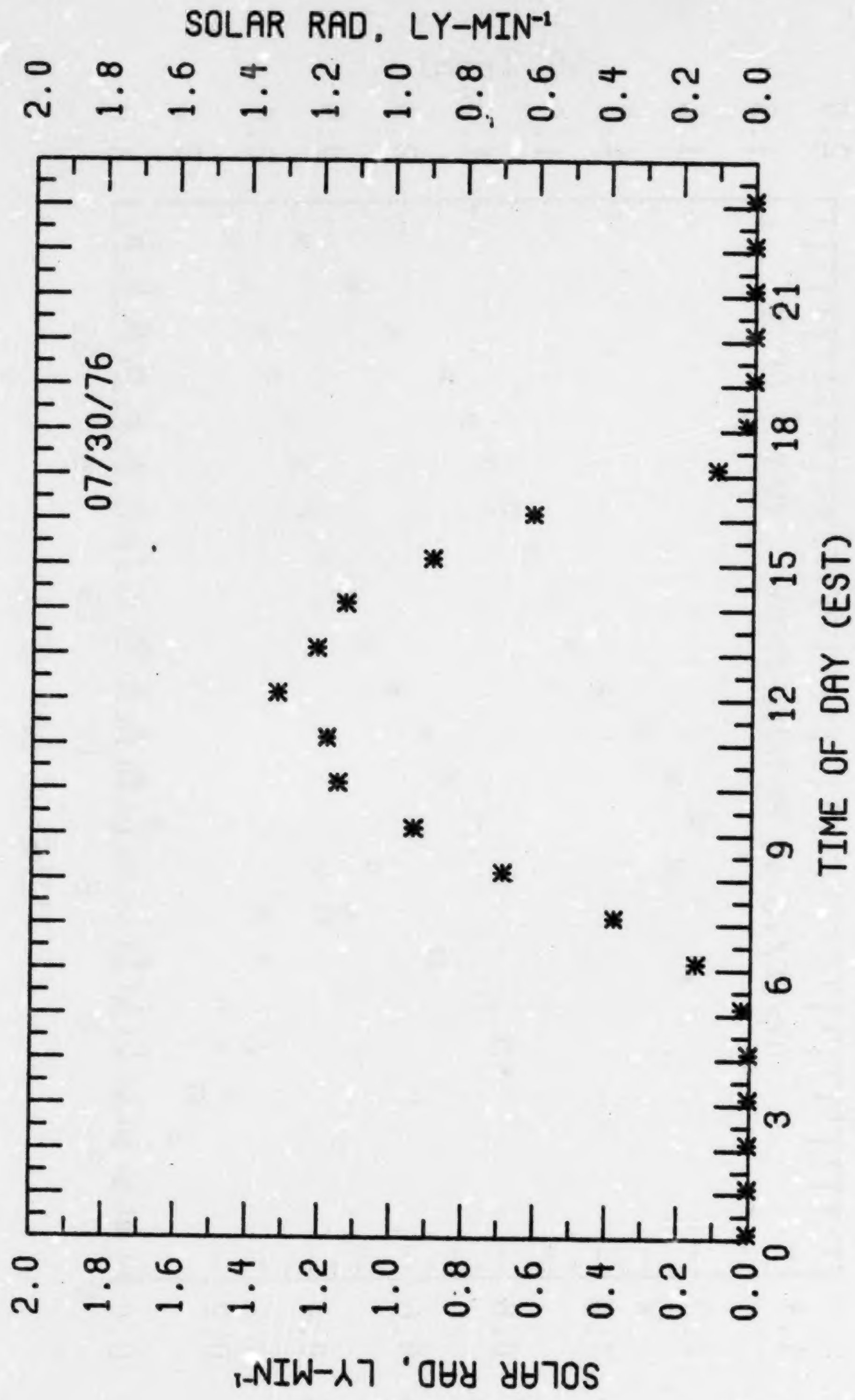

07/13/76 #4 PROPYLENE DAY 1 OF 3
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

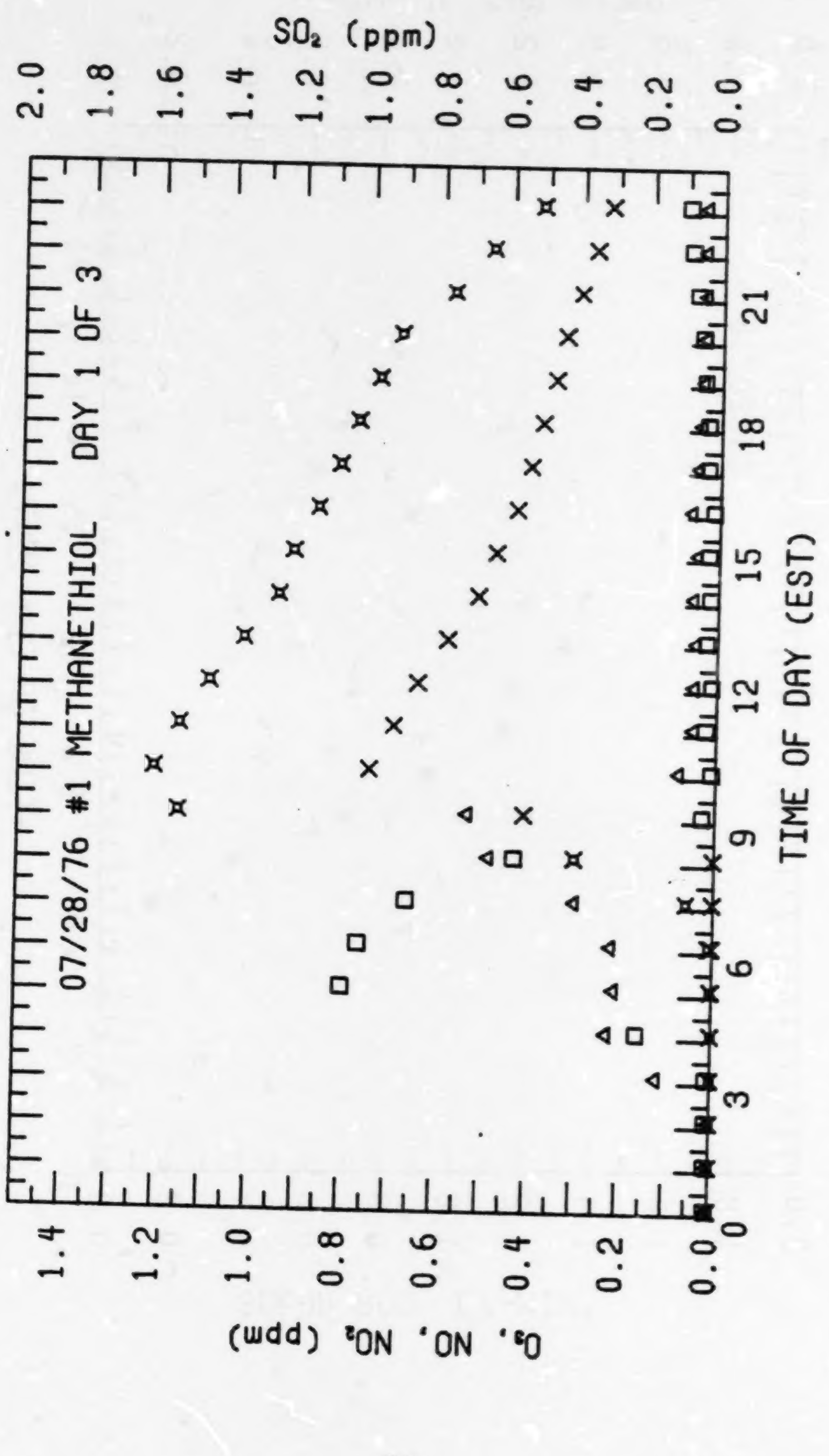

07/14/76 #4 PROPYLENE DAY 2 OF 3
O3, NO, NO2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

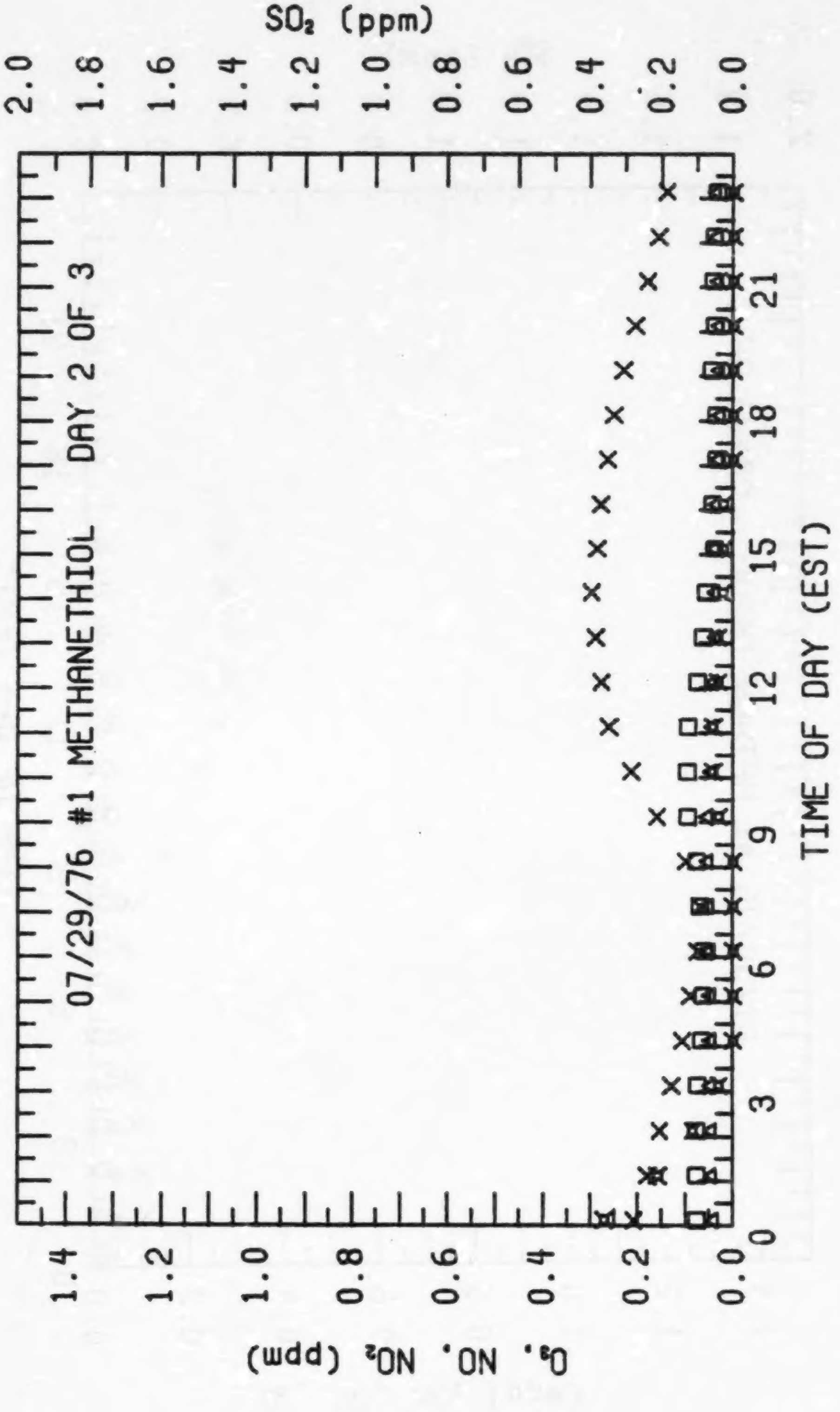

07/15/76 #4 PROPYLENE DAY 3 OF 3
O$_3$, NO, NO$_2$ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

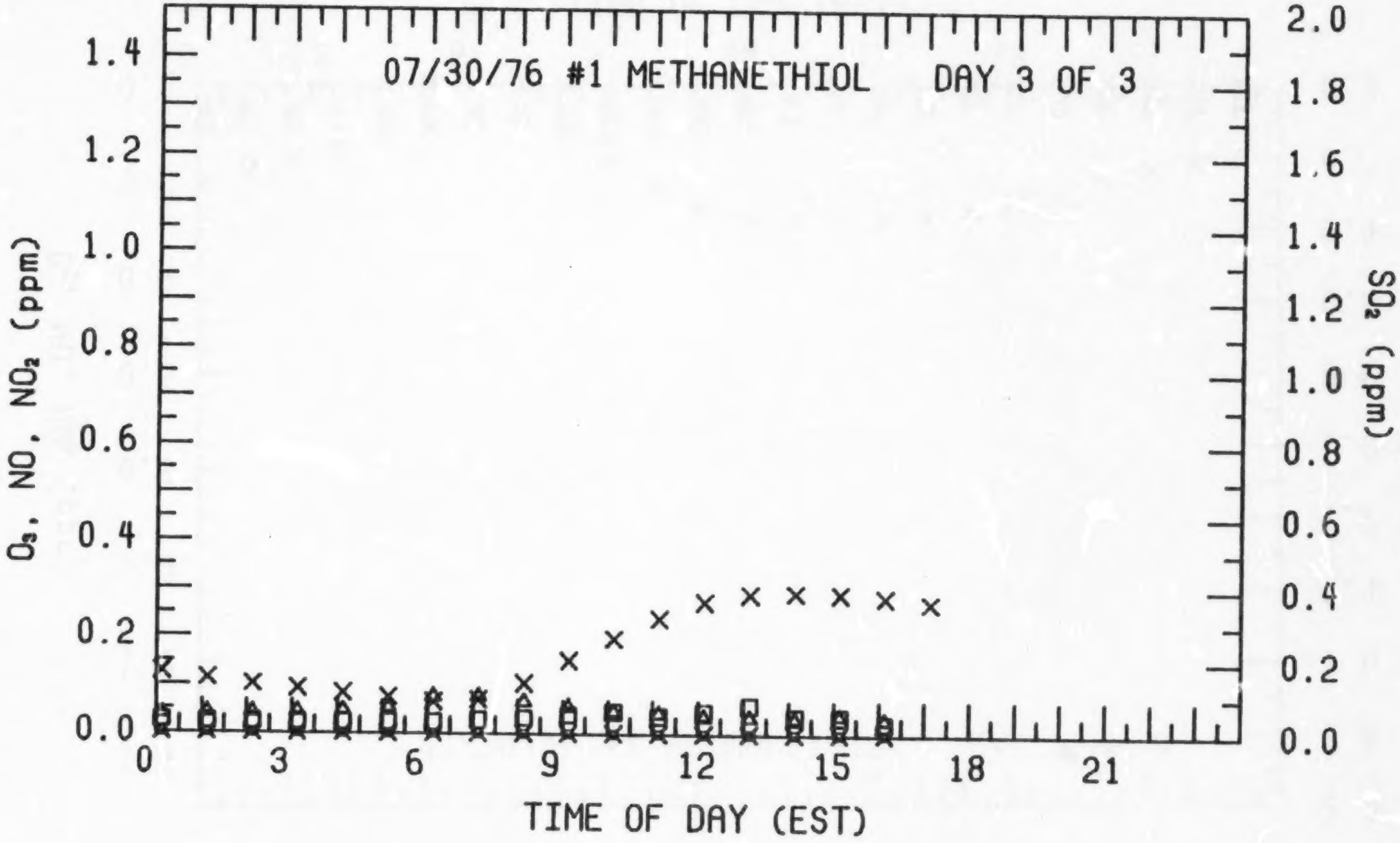

SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
07/28/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN^{-1}

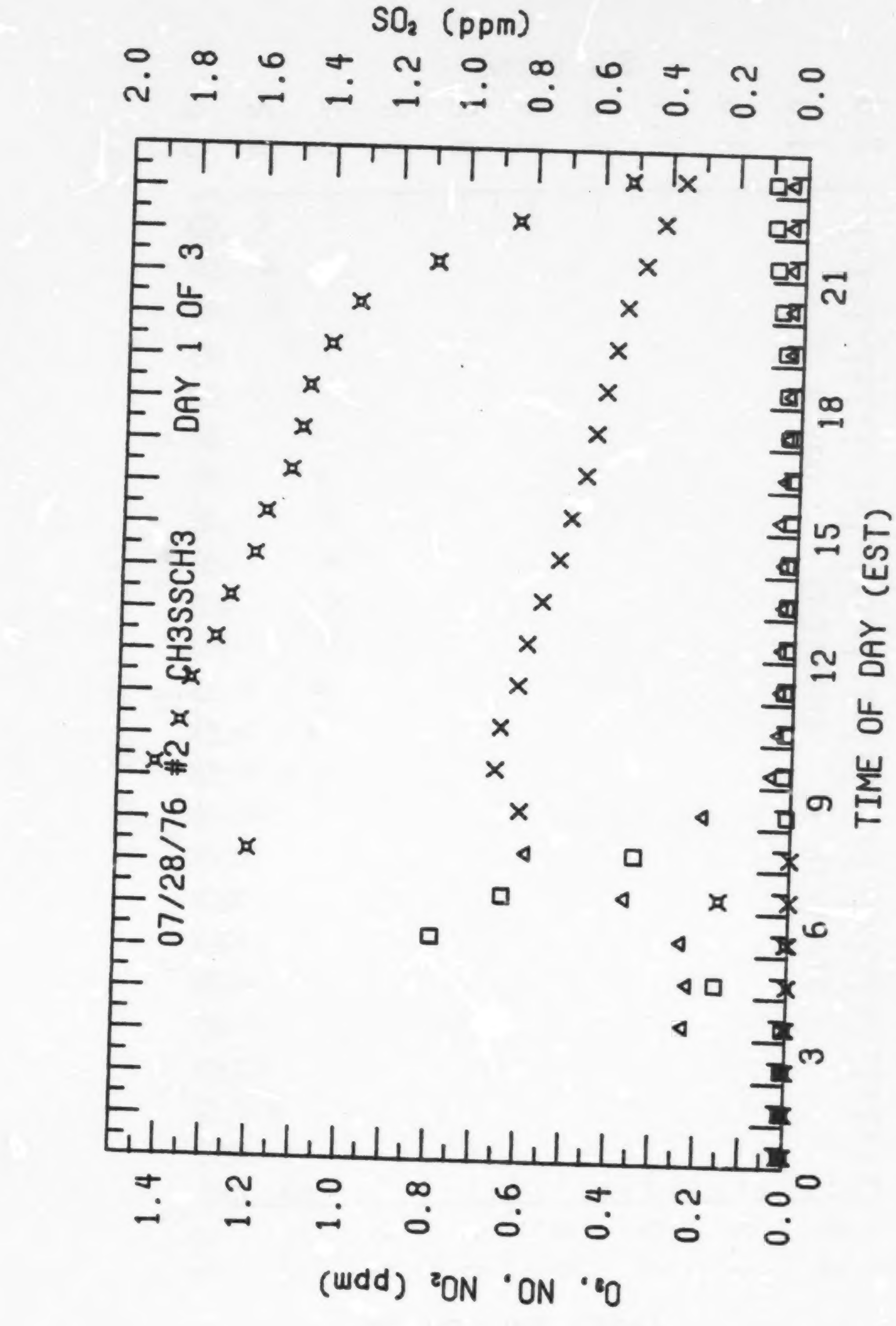

SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
07/29/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN^{-1}

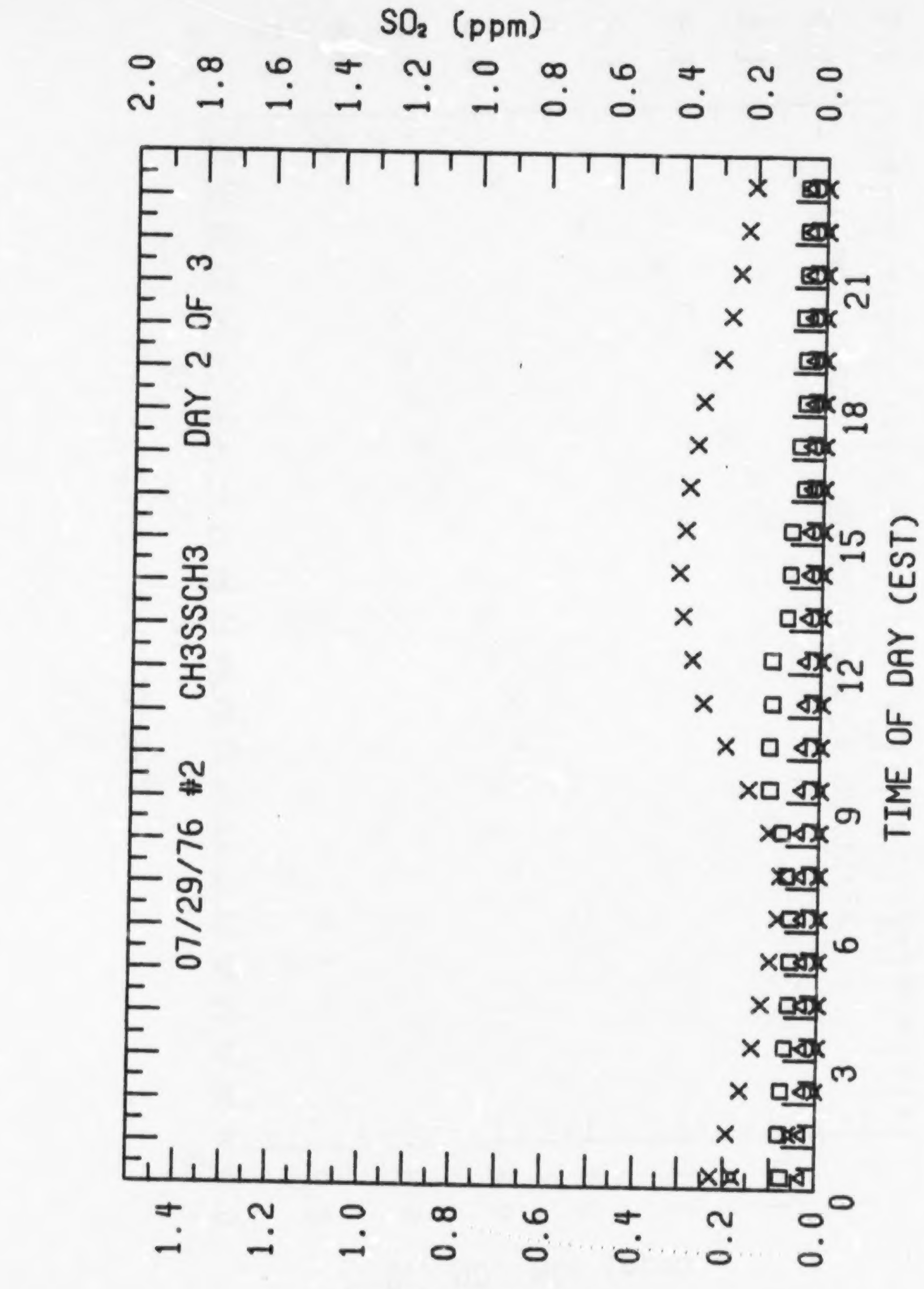

07/30/76
SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

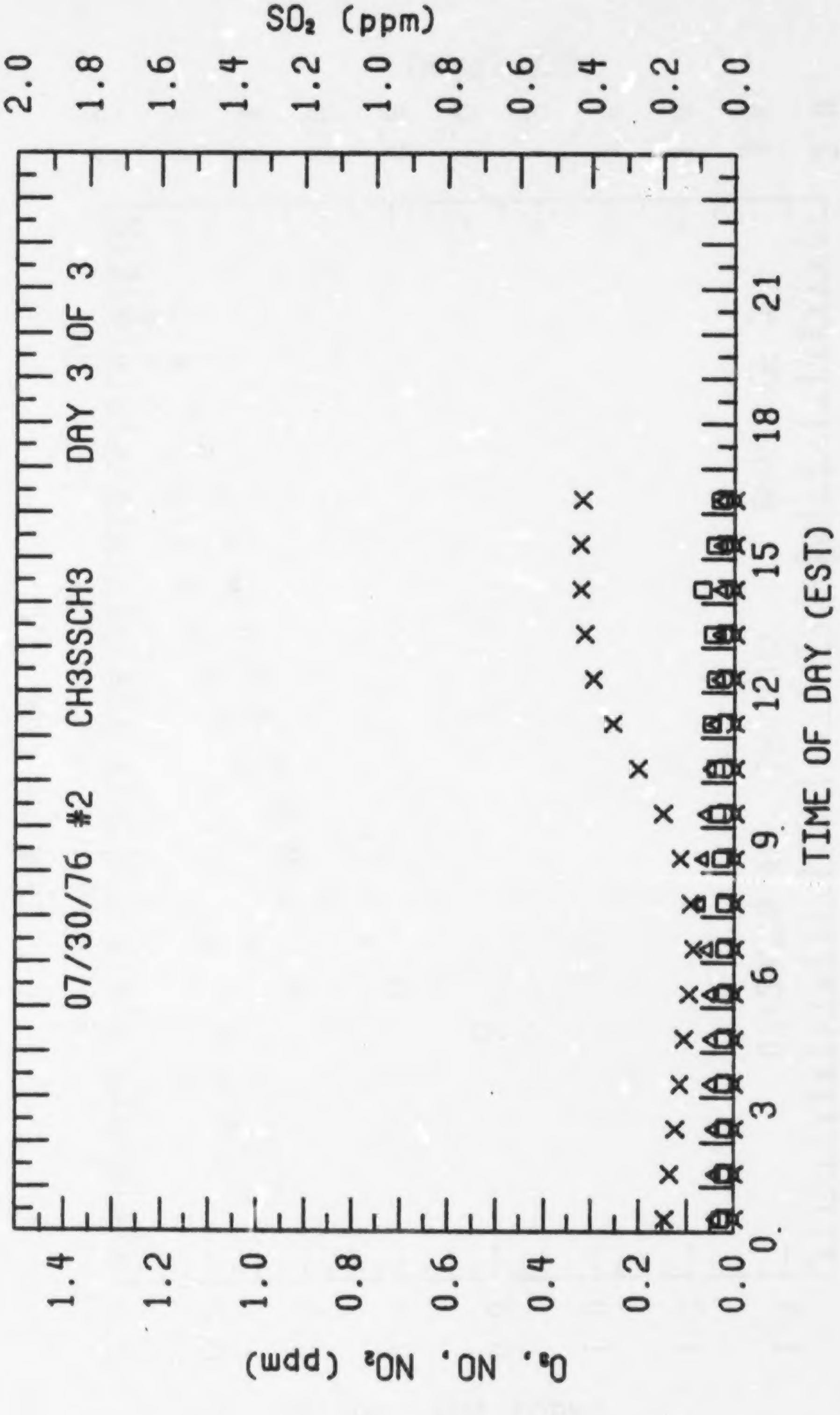

07/28/76 #1 METHANETHIOL DAY 1 OF 3
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

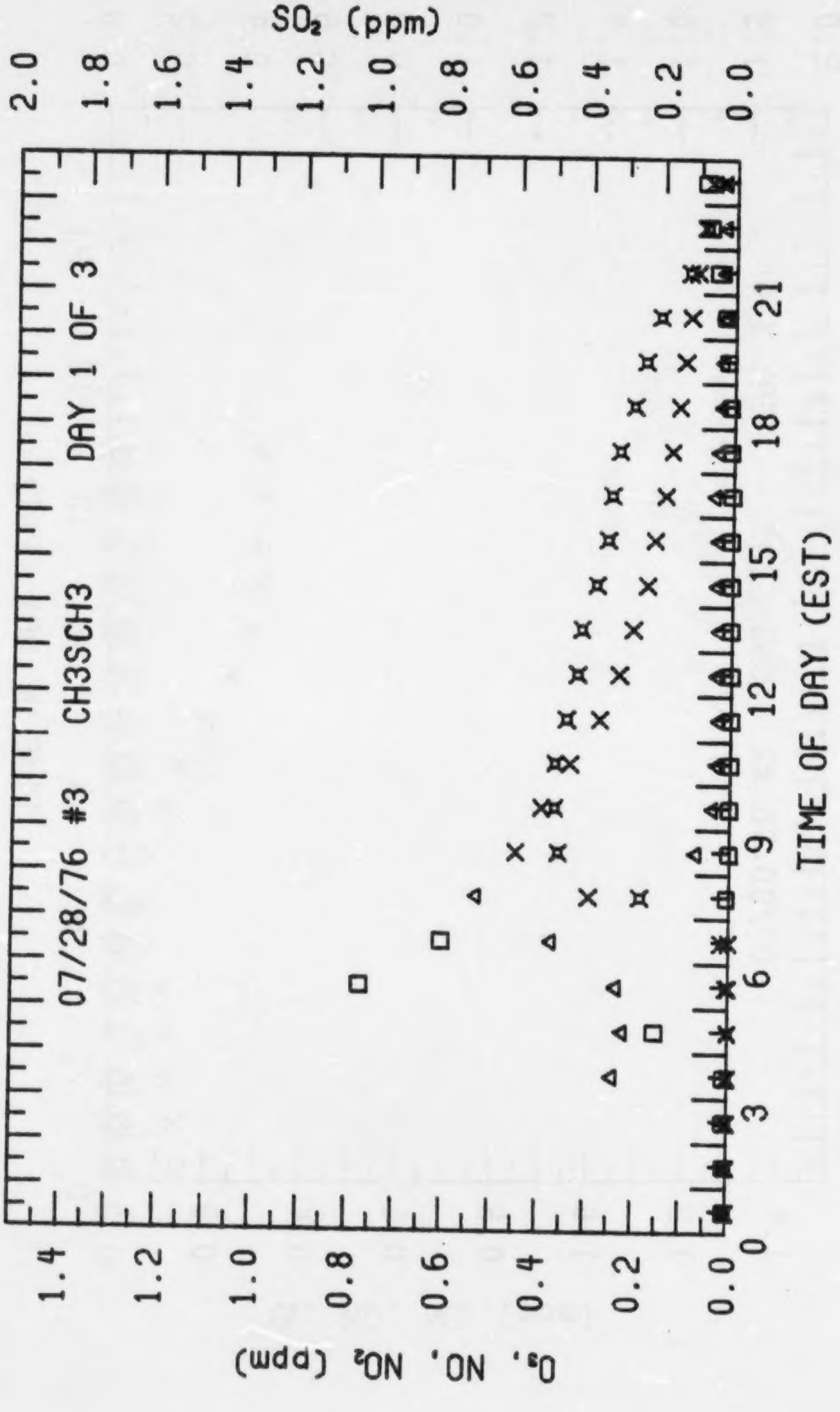

07/29/76 #1 METHANETHIOL DAY 2 OF 3
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

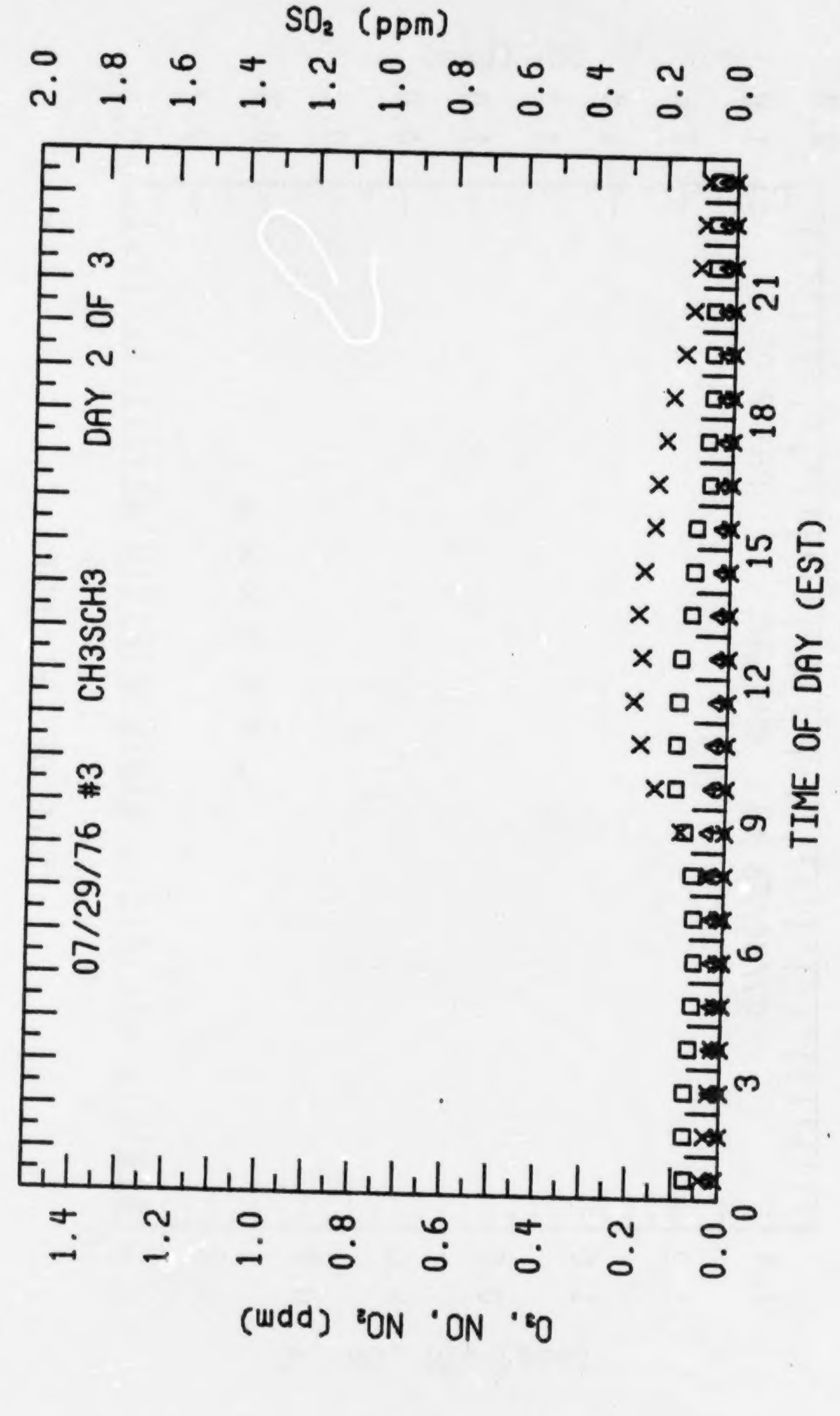

07/30/76 #1 METHANETHIOL DAY 3 OF 3
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
SO_2 (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

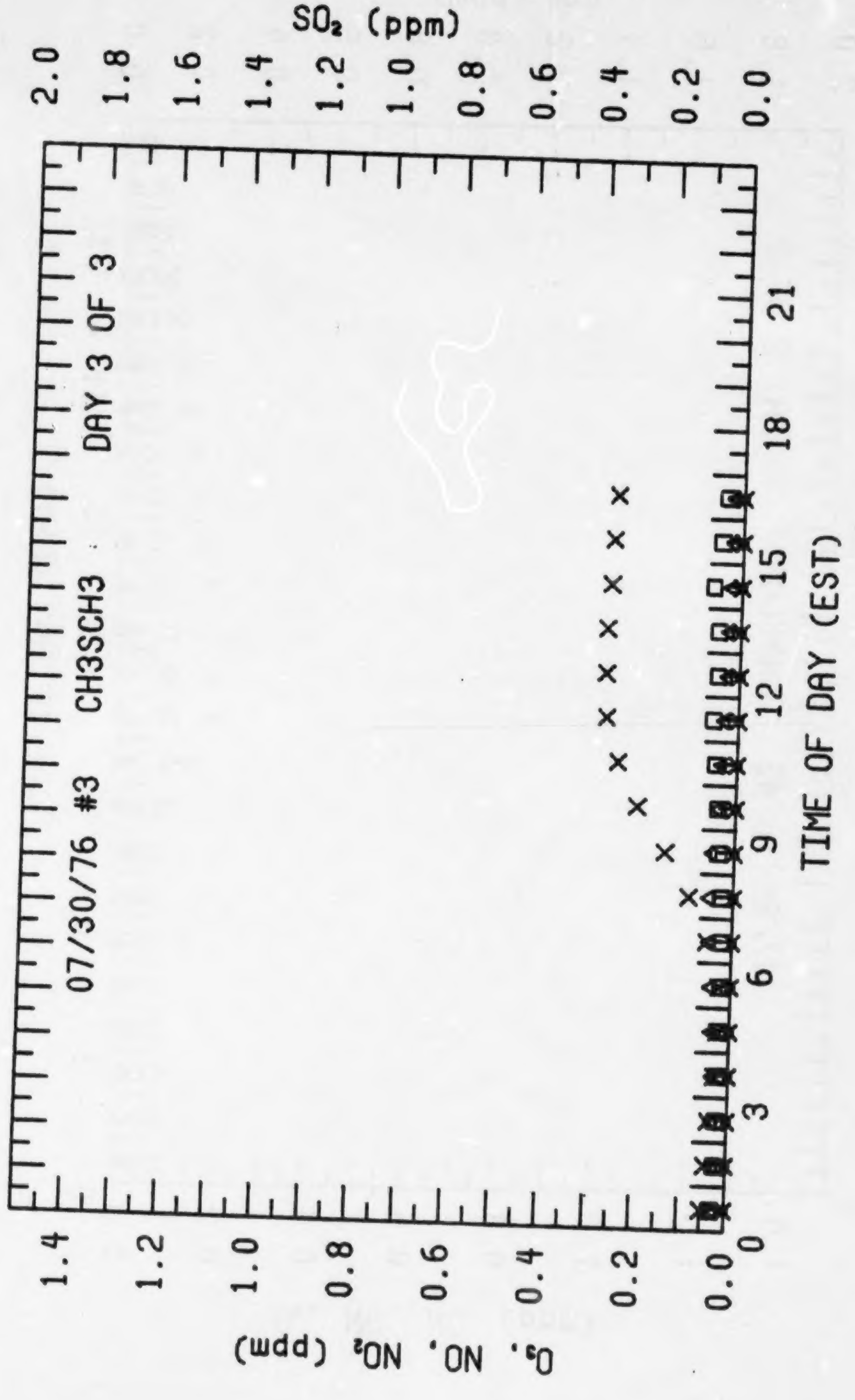

07/28/76 #2 CH3SSCH3 DAY 1 OF 3
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

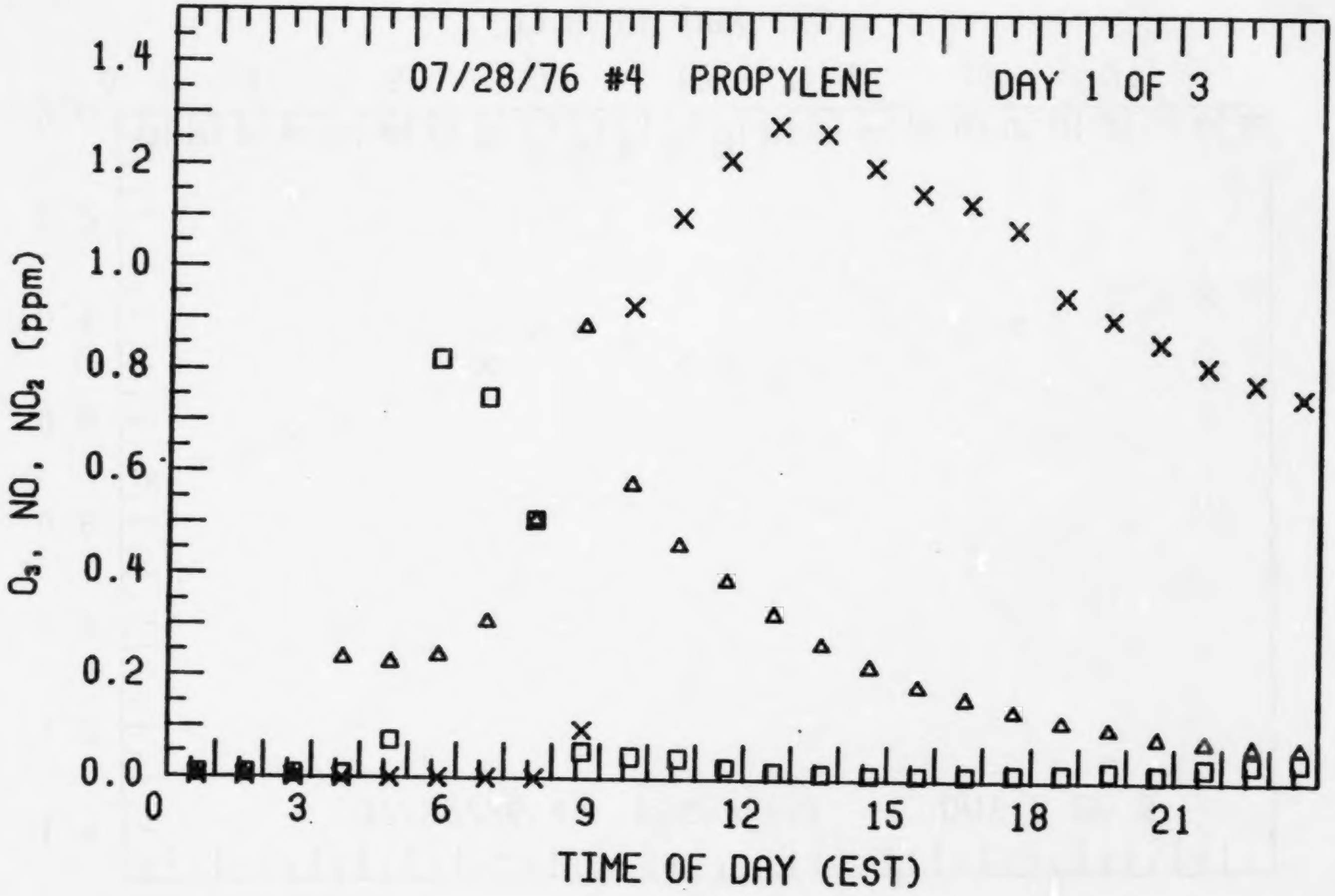

07/29/76 #2
CH3SSCH3
DAY 2 OF 3
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

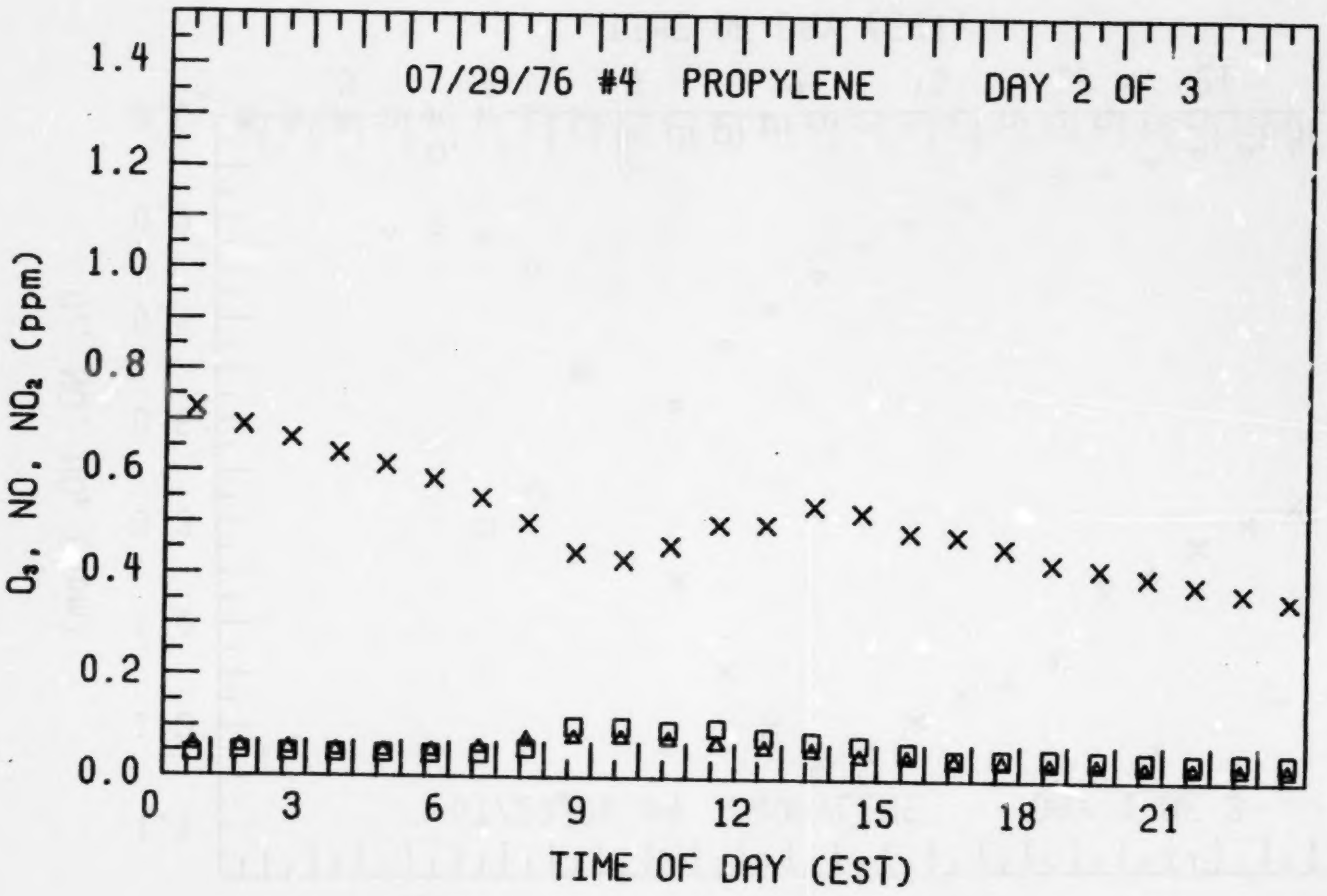

07/30/76 #2
CH3SSCH3
DAY 3 OF 3
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.
3
6
9
12
15
18
21
TIME OF DAY (EST)

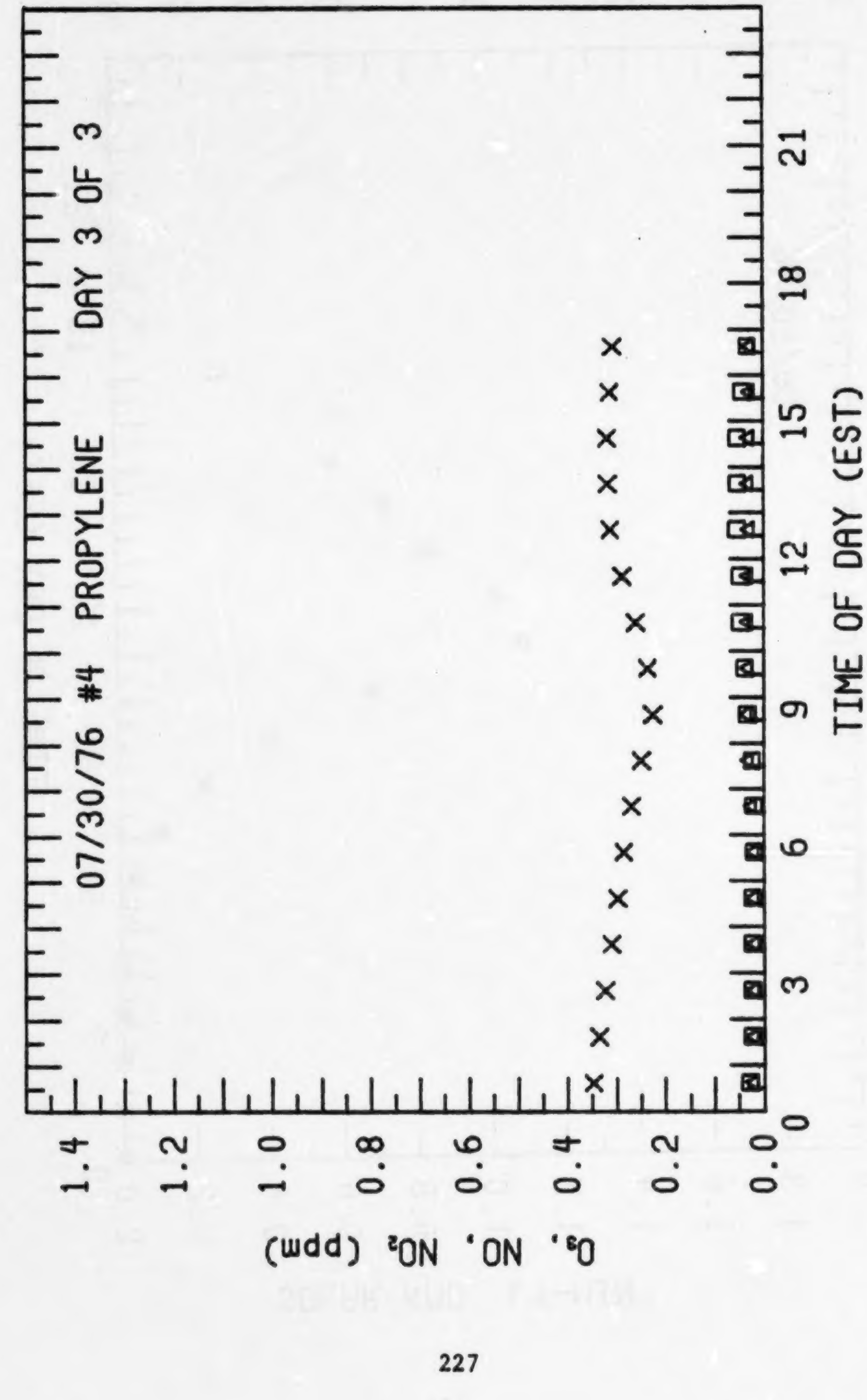

07/28/76 #3
CH3SCH3
DAY 1 OF 3
TIME OF DAY (EST)
0
3
6
9
12
15
18
21
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

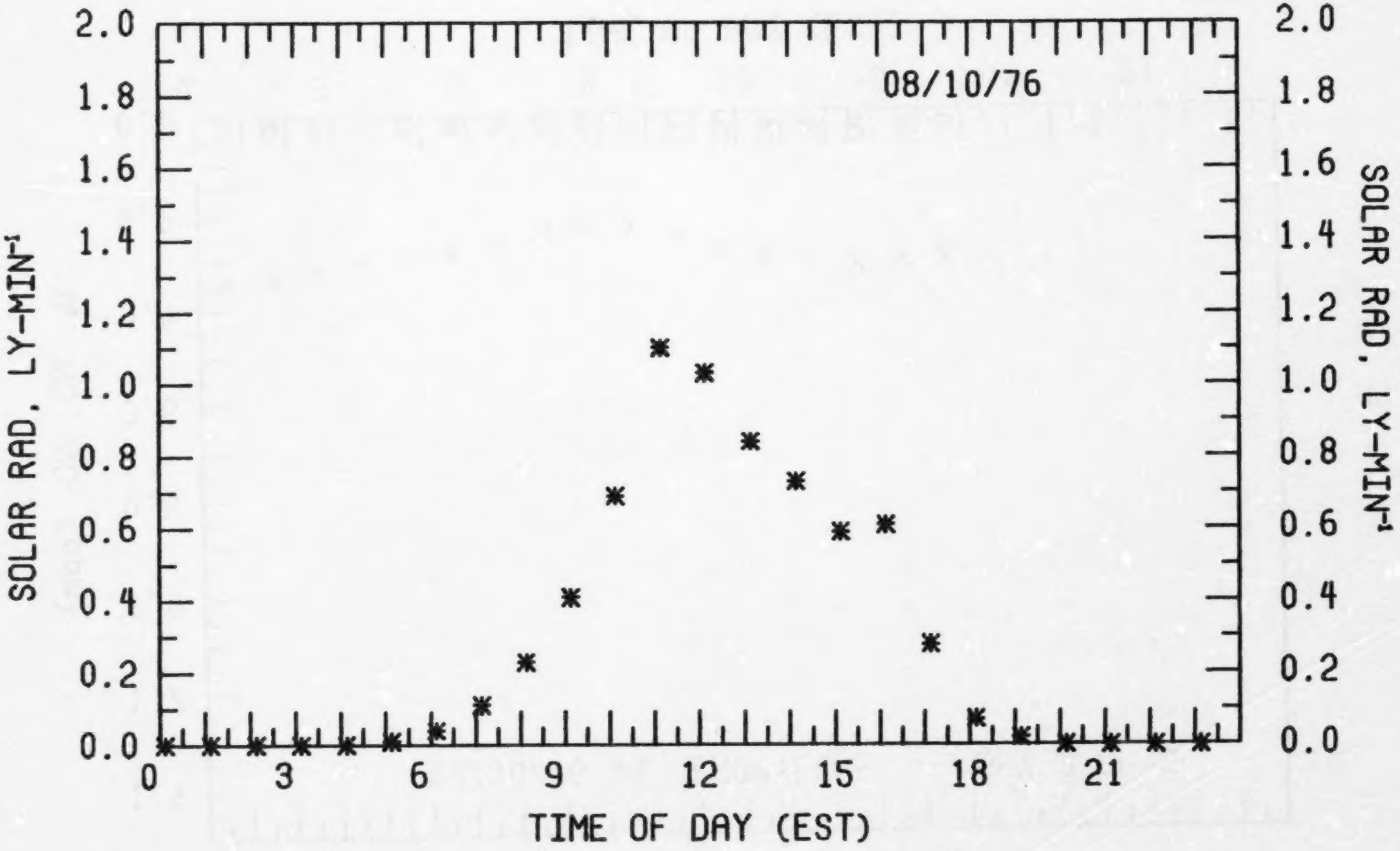

07/29/76 #3
CH3SCH3
DAY 2 OF 3
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

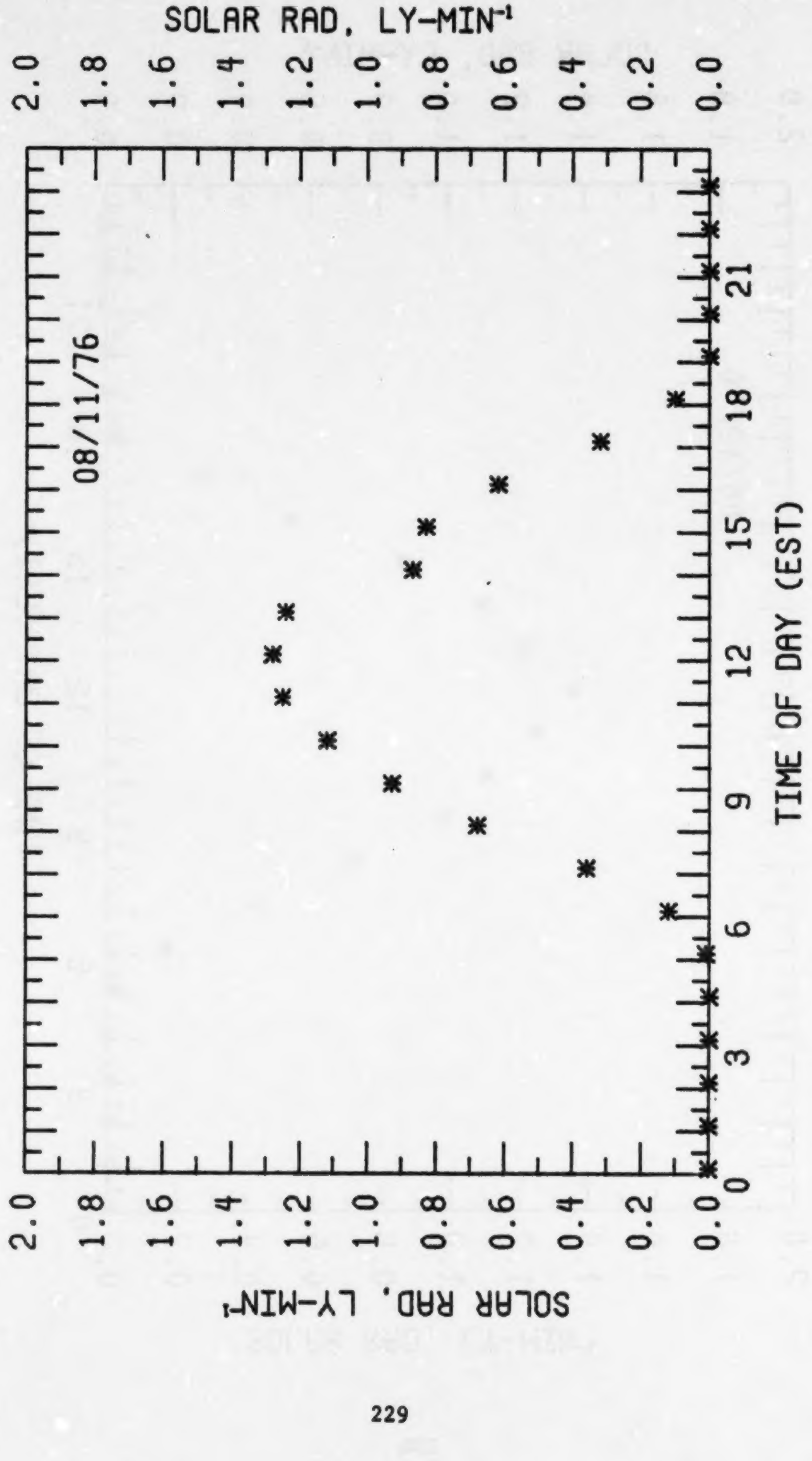

07/30/76 #3
CH3SCH3
DAY 3 OF 3
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

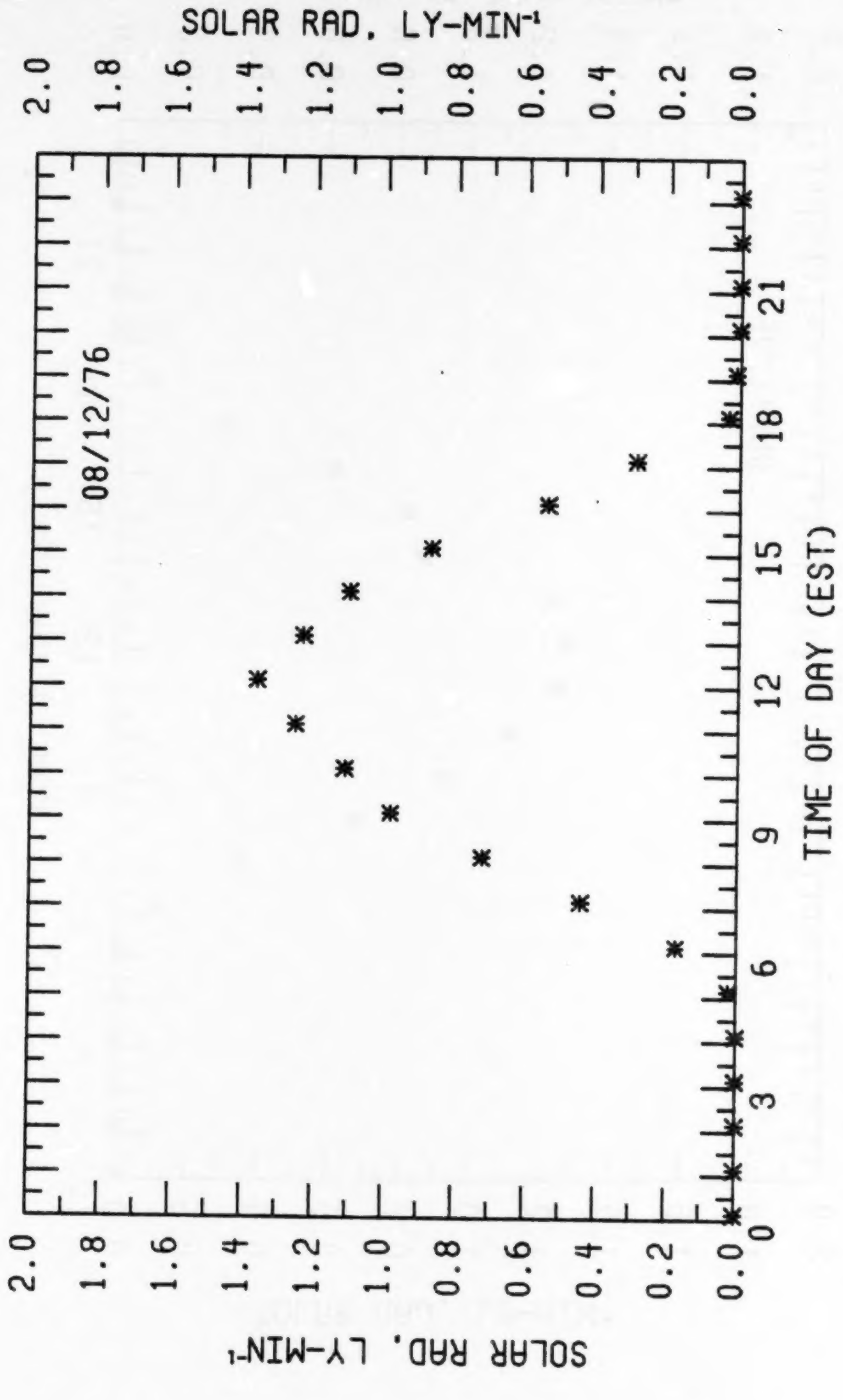

07/28/76 #4 PROPYLENE DAY 1 OF 3
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

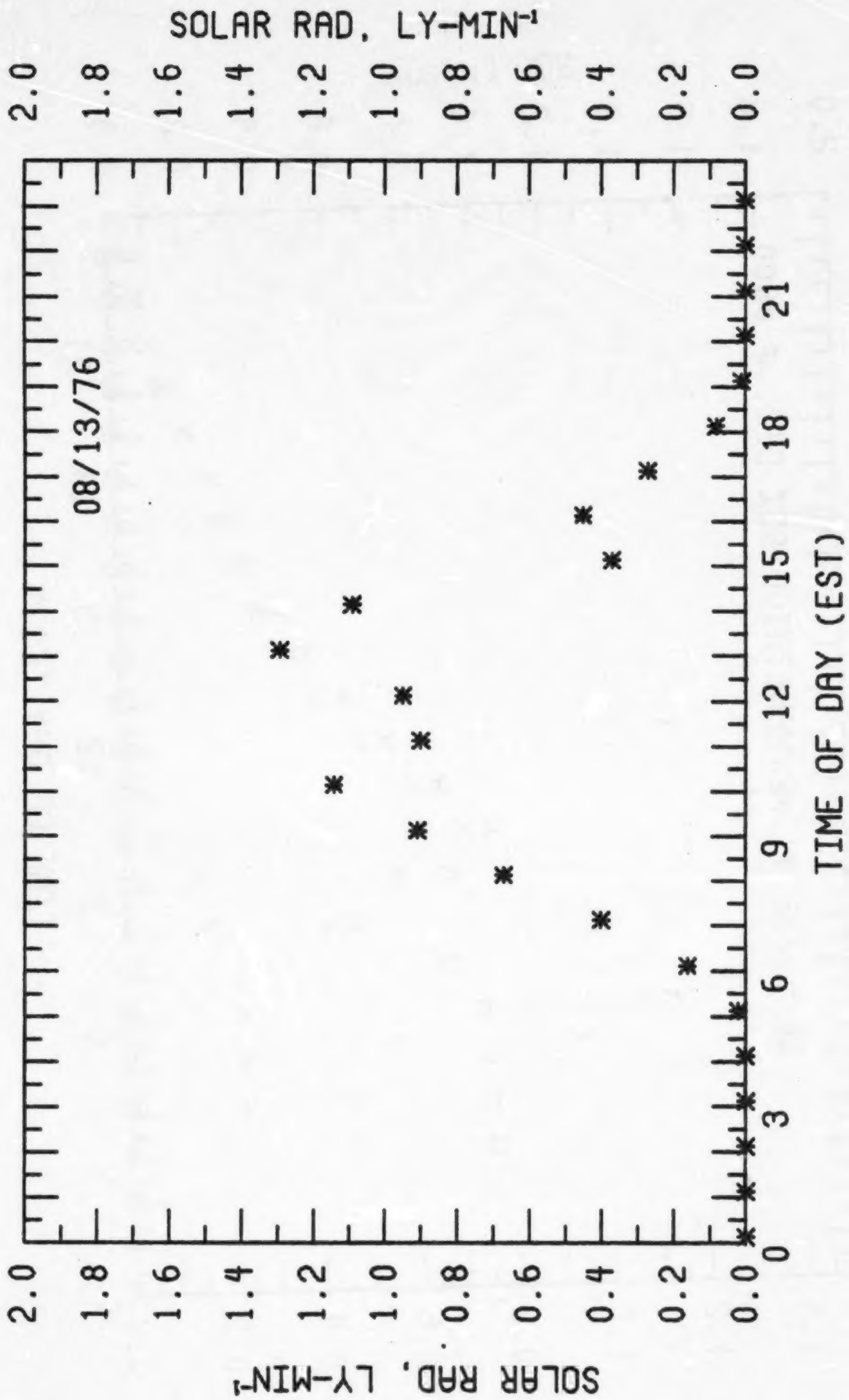

07/29/76 #4 PROPYLENE DAY 2 OF 3
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

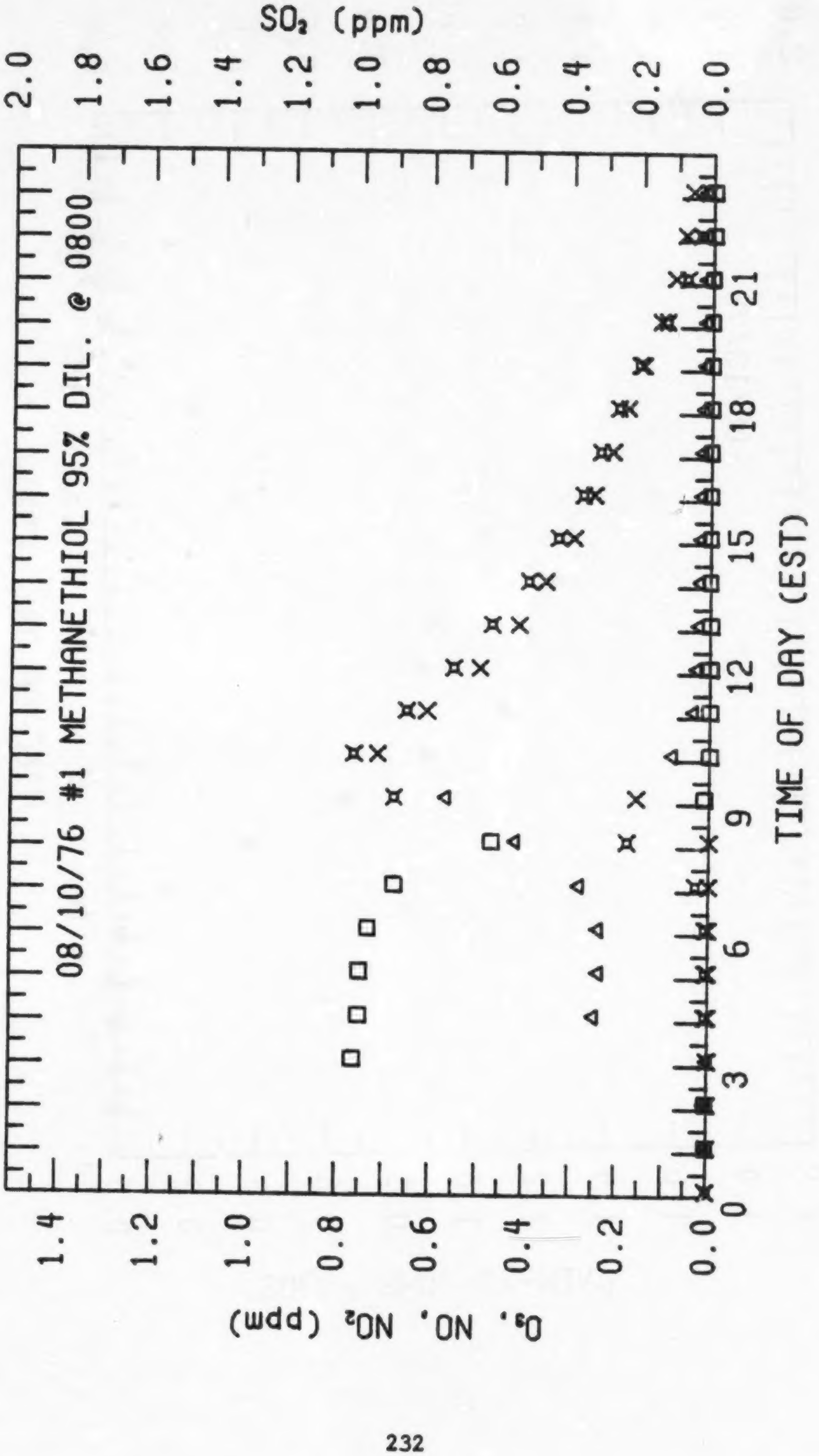

07/30/76 #4 PROPYLENE DAY 3 OF 3
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

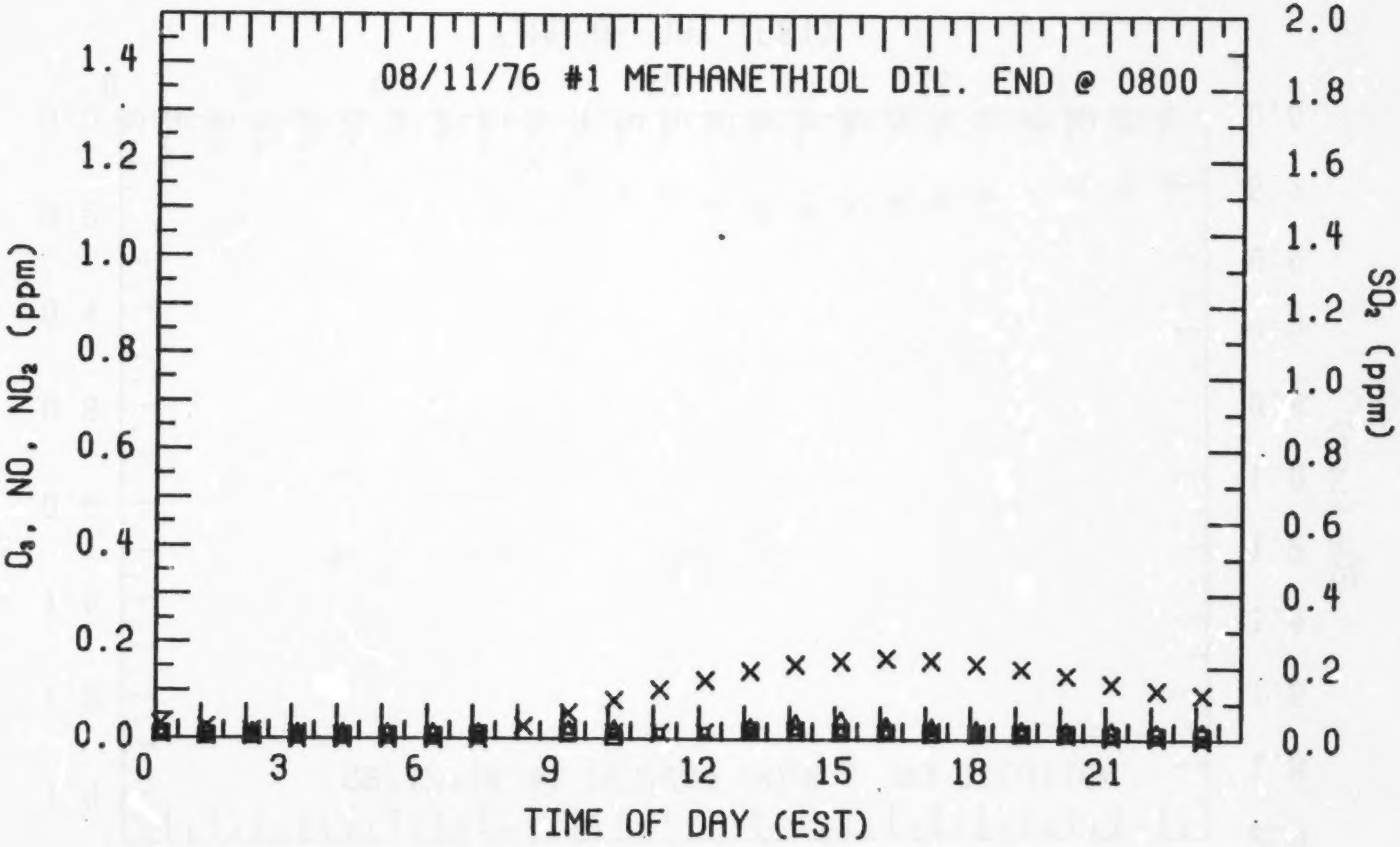

08/10/76
SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

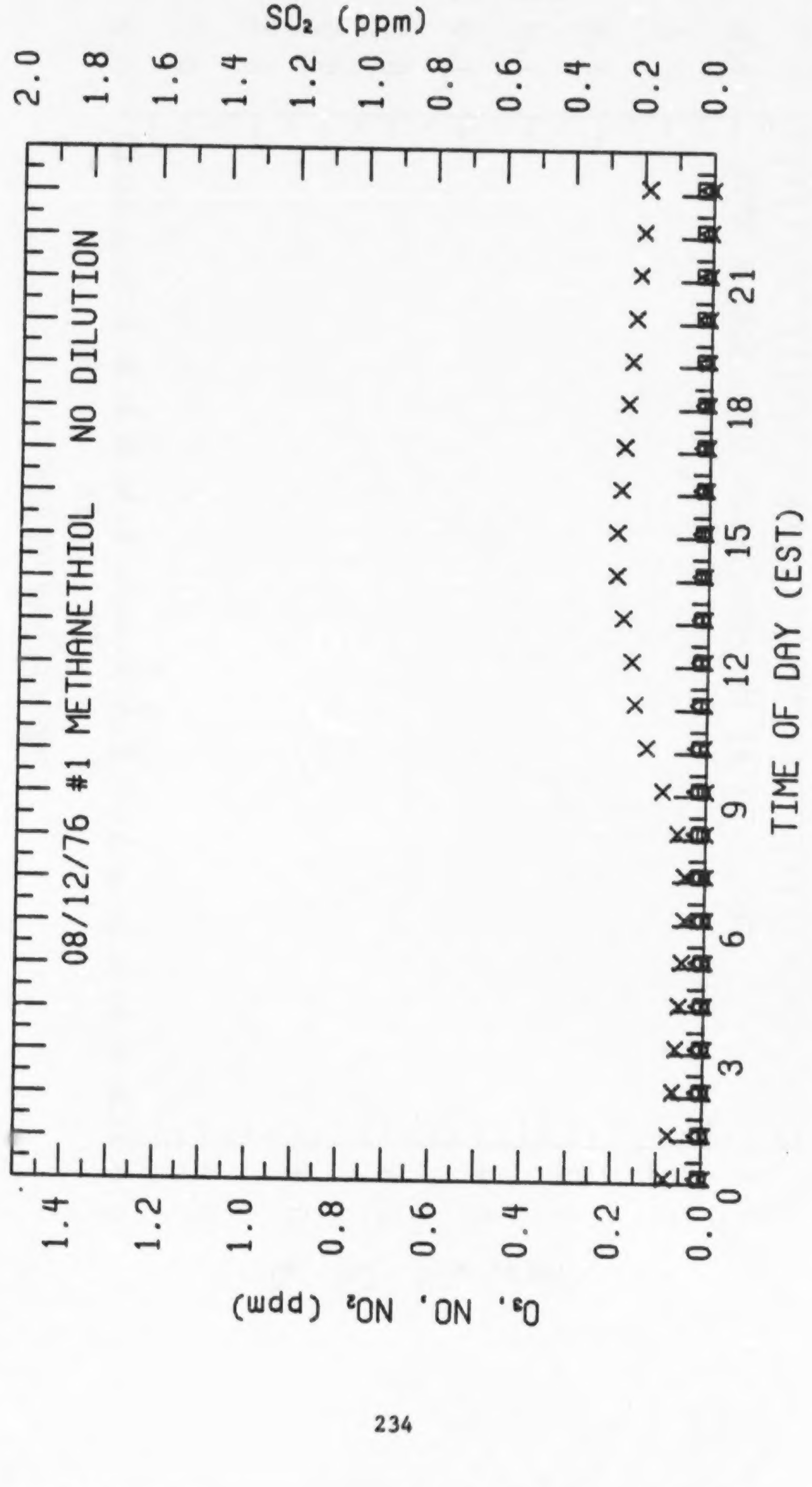

SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
08/11/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN^{-1}


SOLAR RAD, LY-MIN⁻¹
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
08/12/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN⁻¹

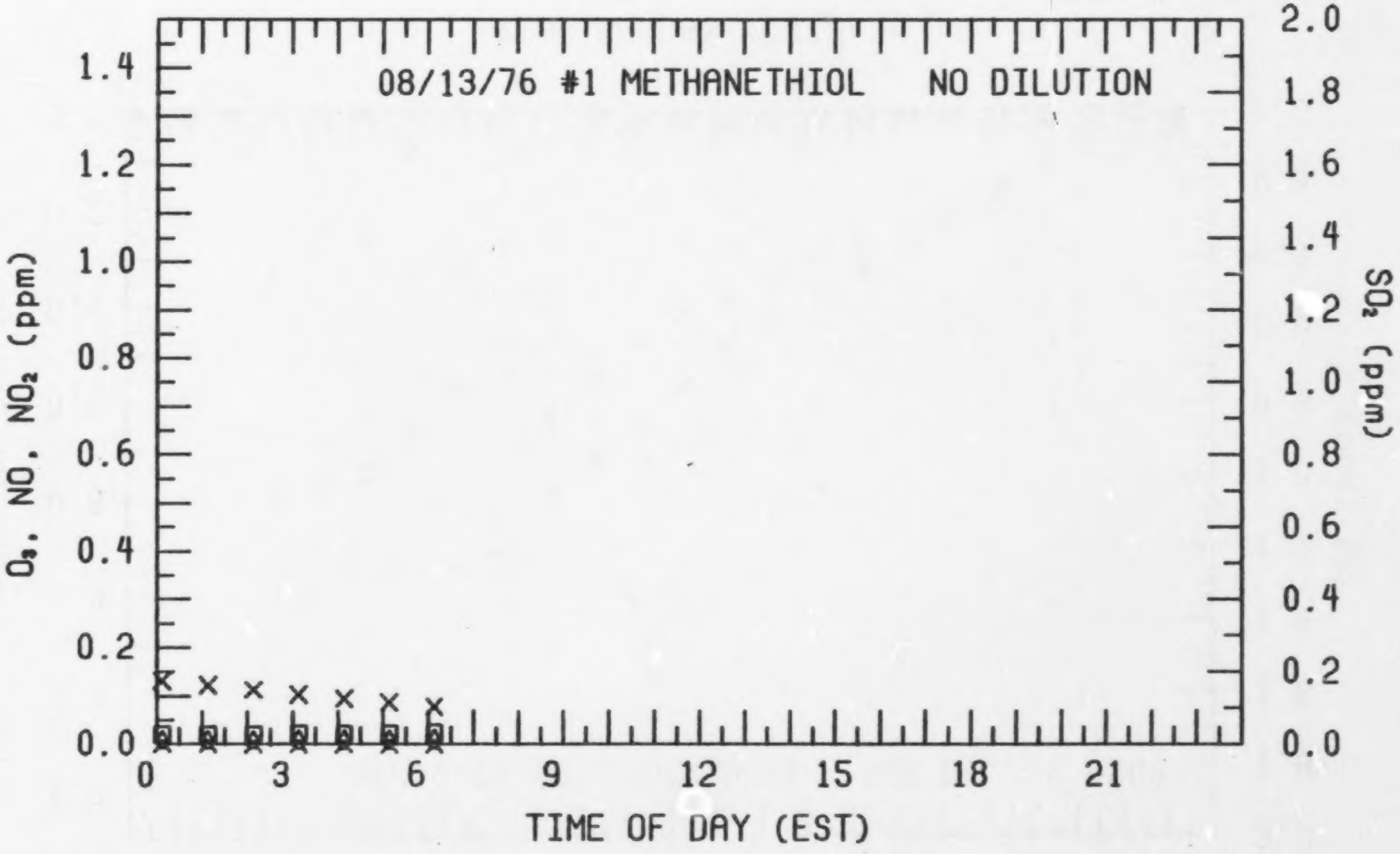

SOLAR RAD, LY-MIN^{-1}
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
08/13/76
0
3
6
9
12
15
18
21
TIME OF DAY (EST)
SOLAR RAD, LY-MIN^{-1}

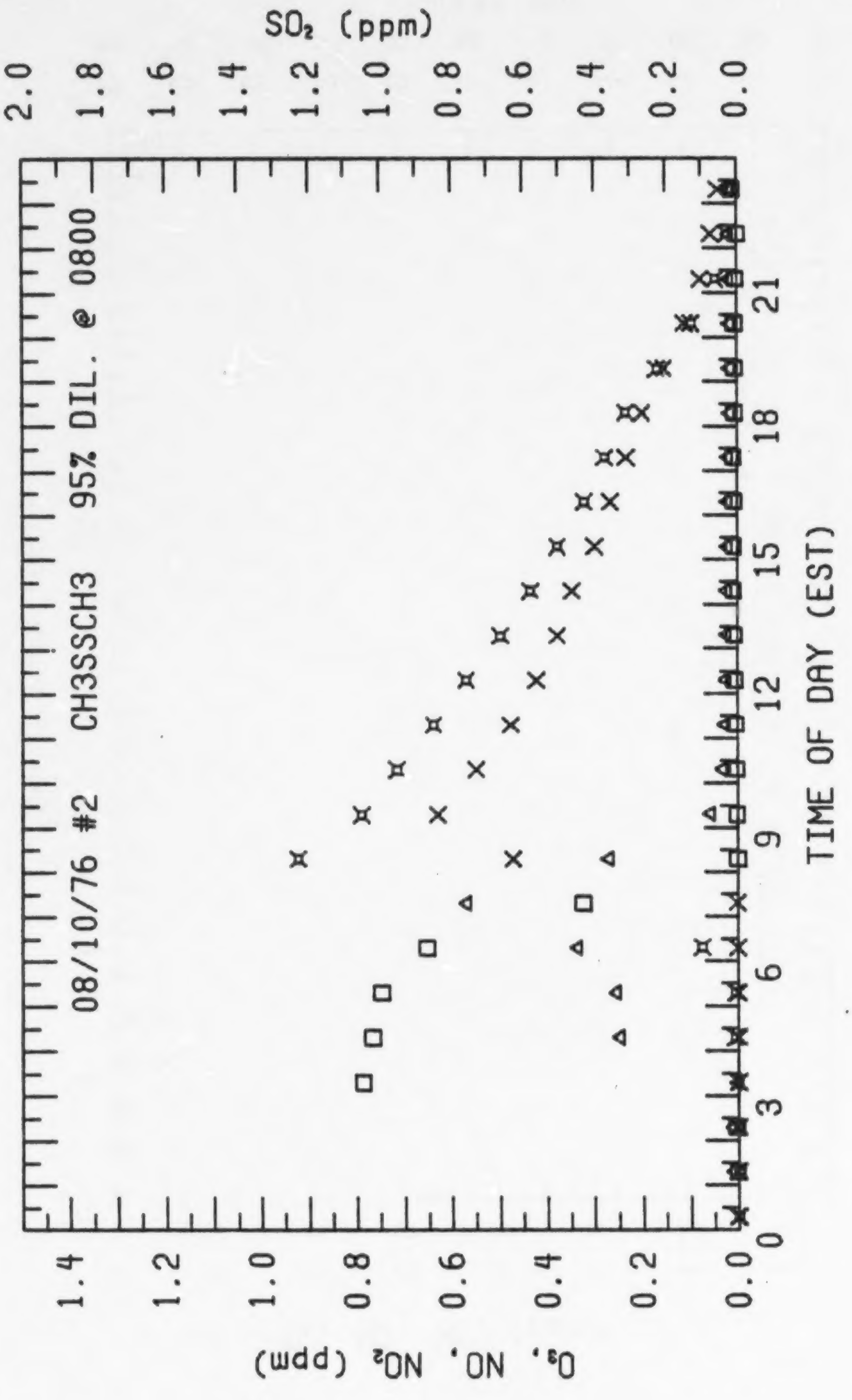

08/10/76 #1 METHANETHIOL 95% DIL. @ 0800
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

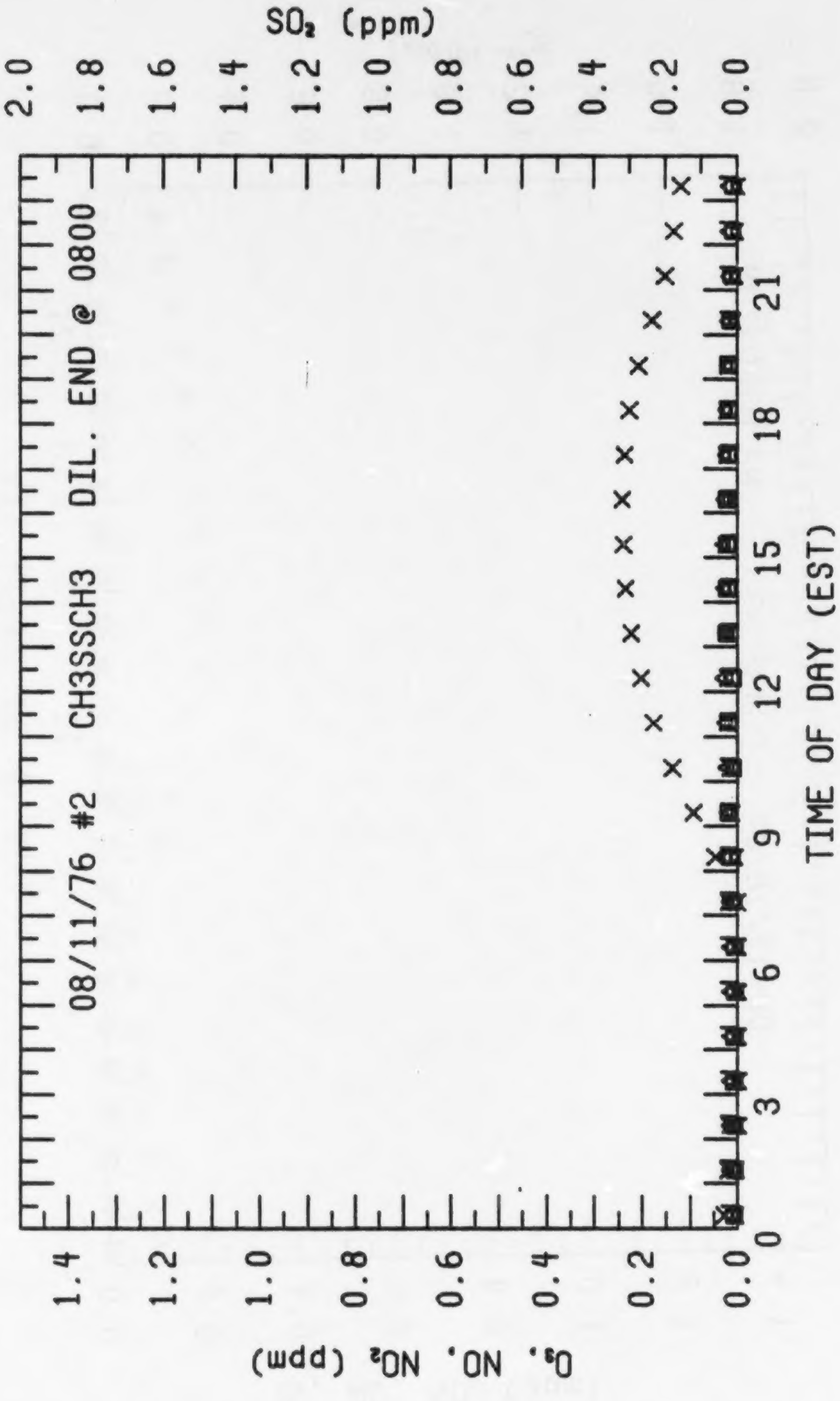

08/11/76 #1 METHANETHIOL DIL. END @ 0800
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
SO_2 (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

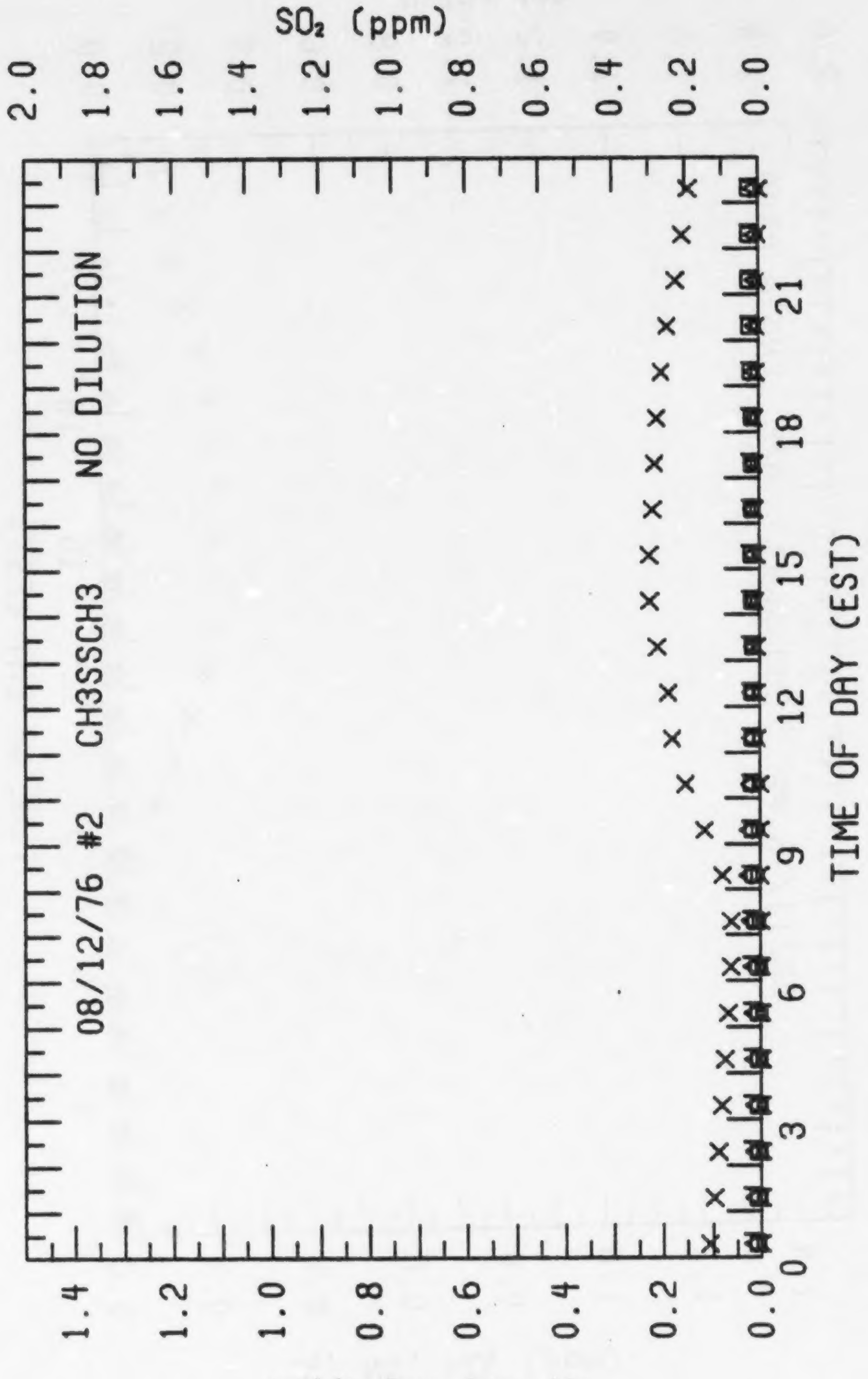


08/12/76 #1 METHANETHIOL NO DILUTION
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

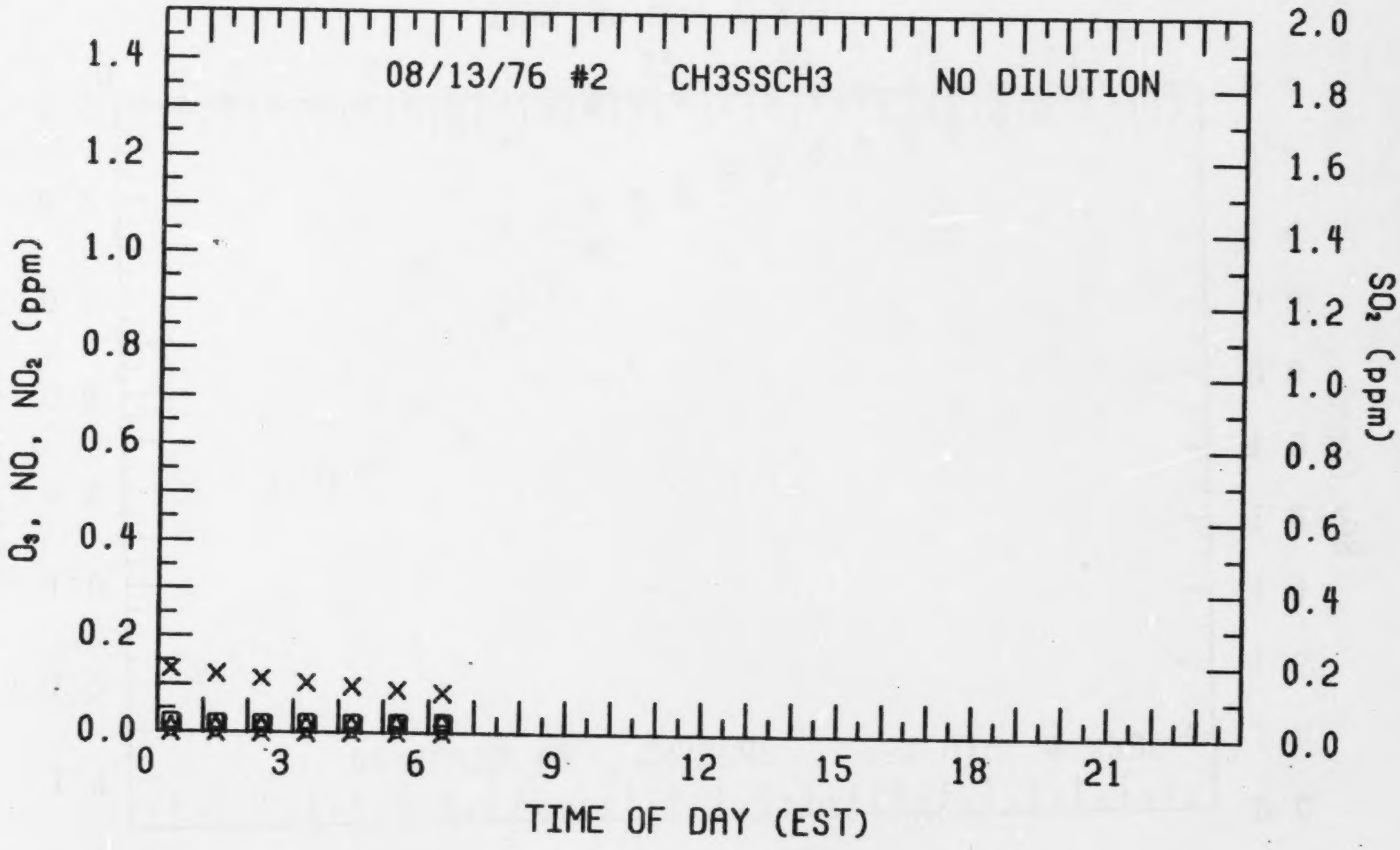

08/13/76 #1 METHANETHIOL NO DILUTION
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
SO_2 (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

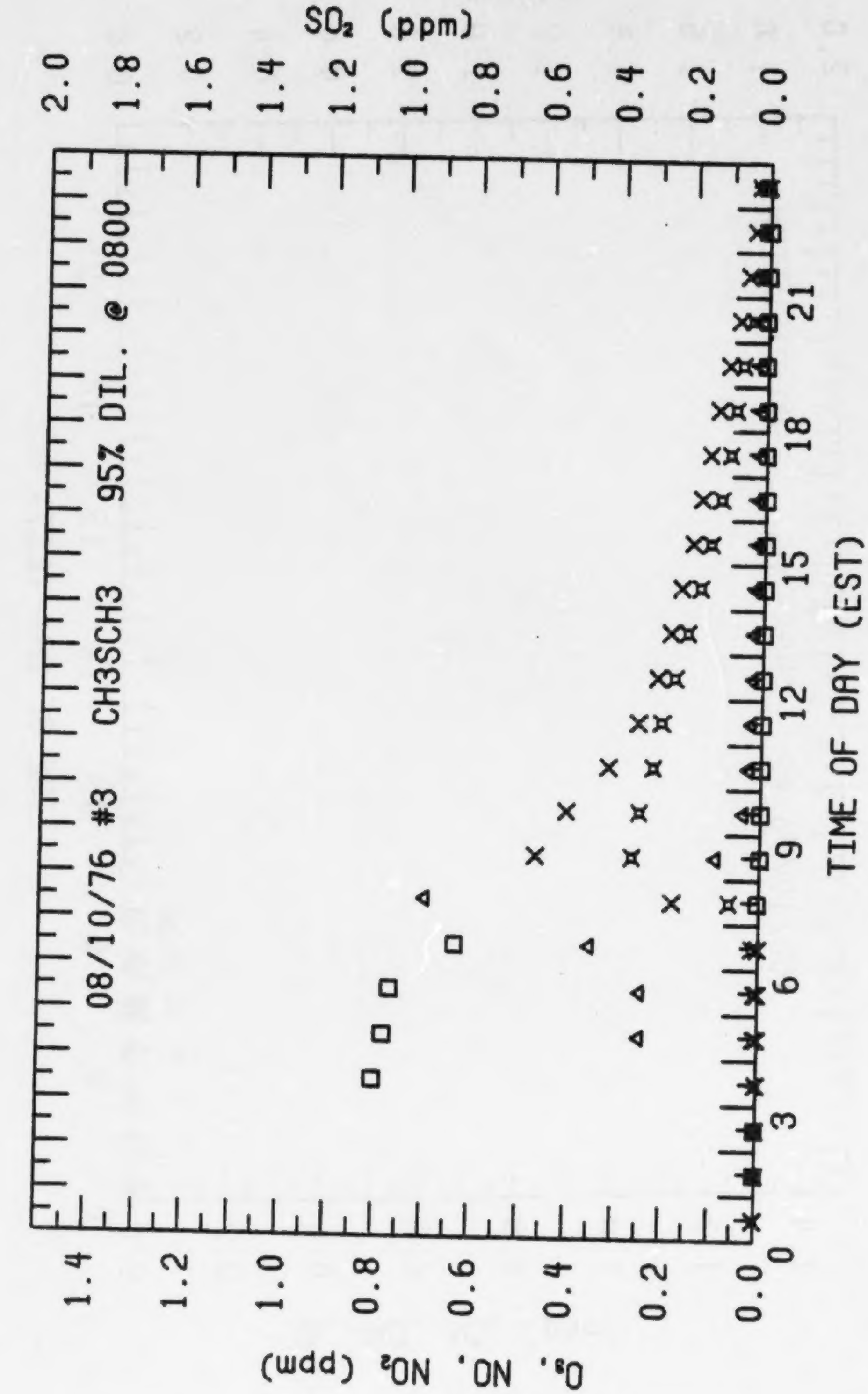

08/10/76 #2 CH3SSCH3 95% DIL. @ 0800
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

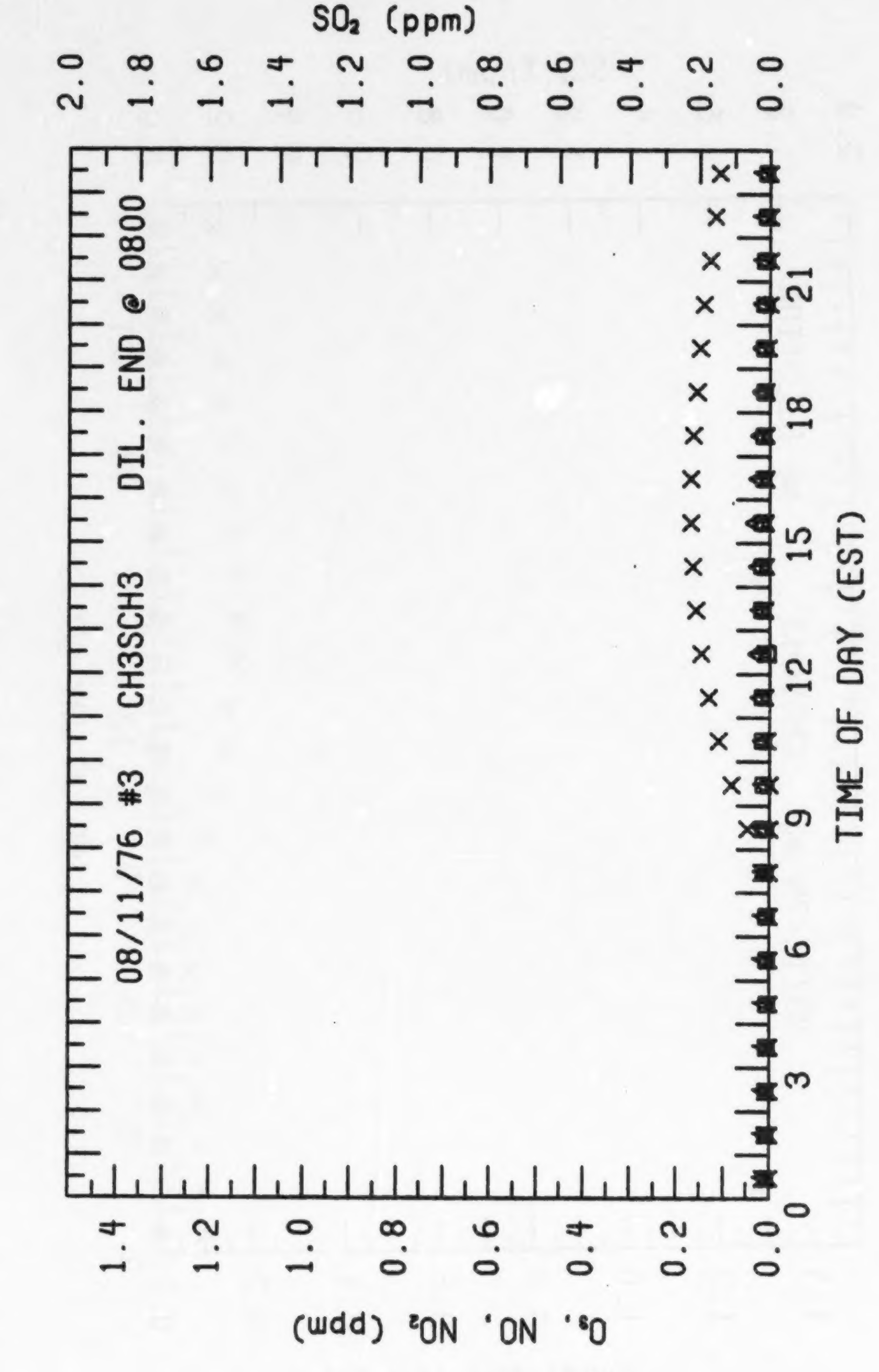

08/11/76 #2 CH3SSCH3 DIL. END @ 0800
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

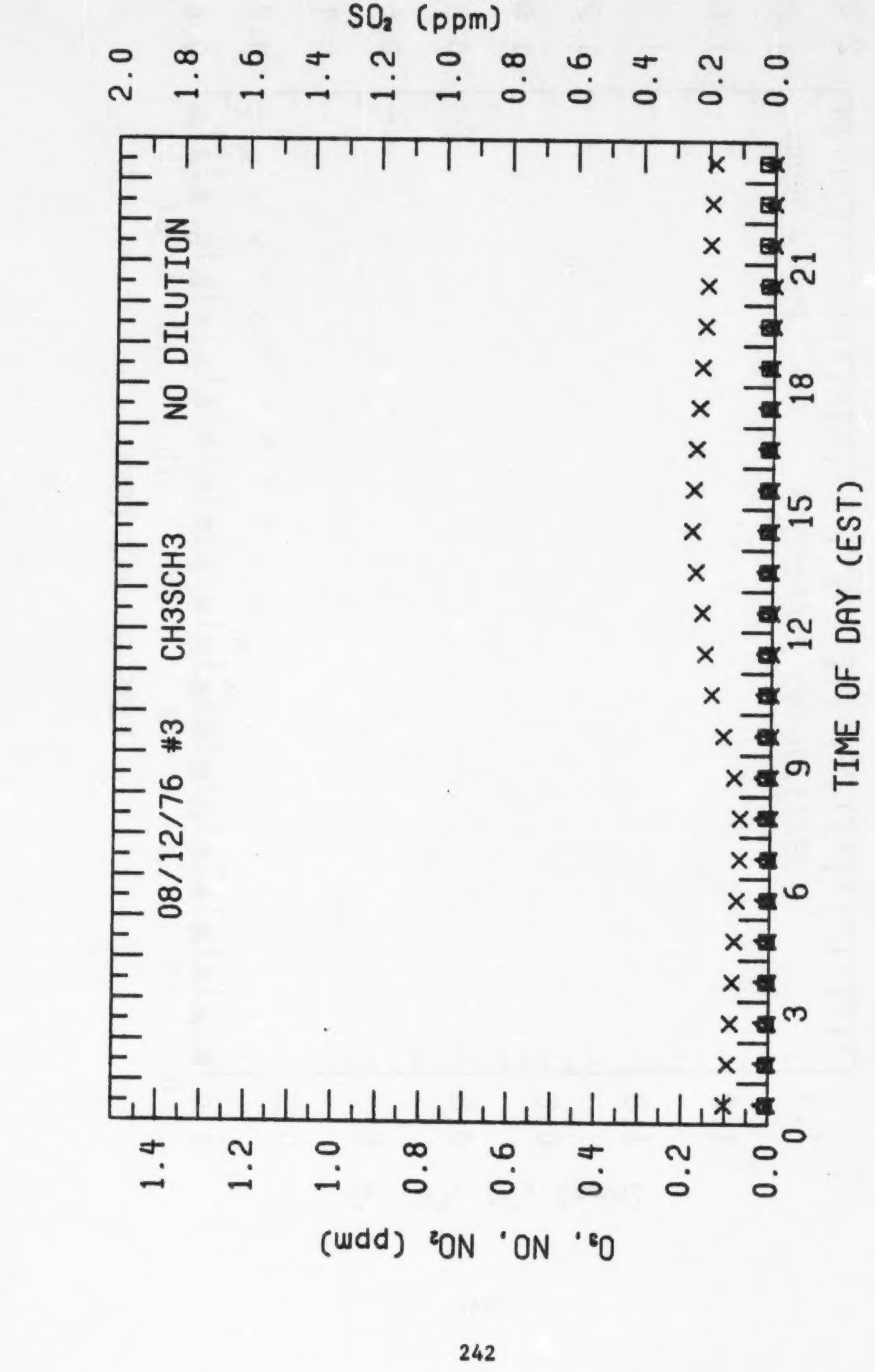


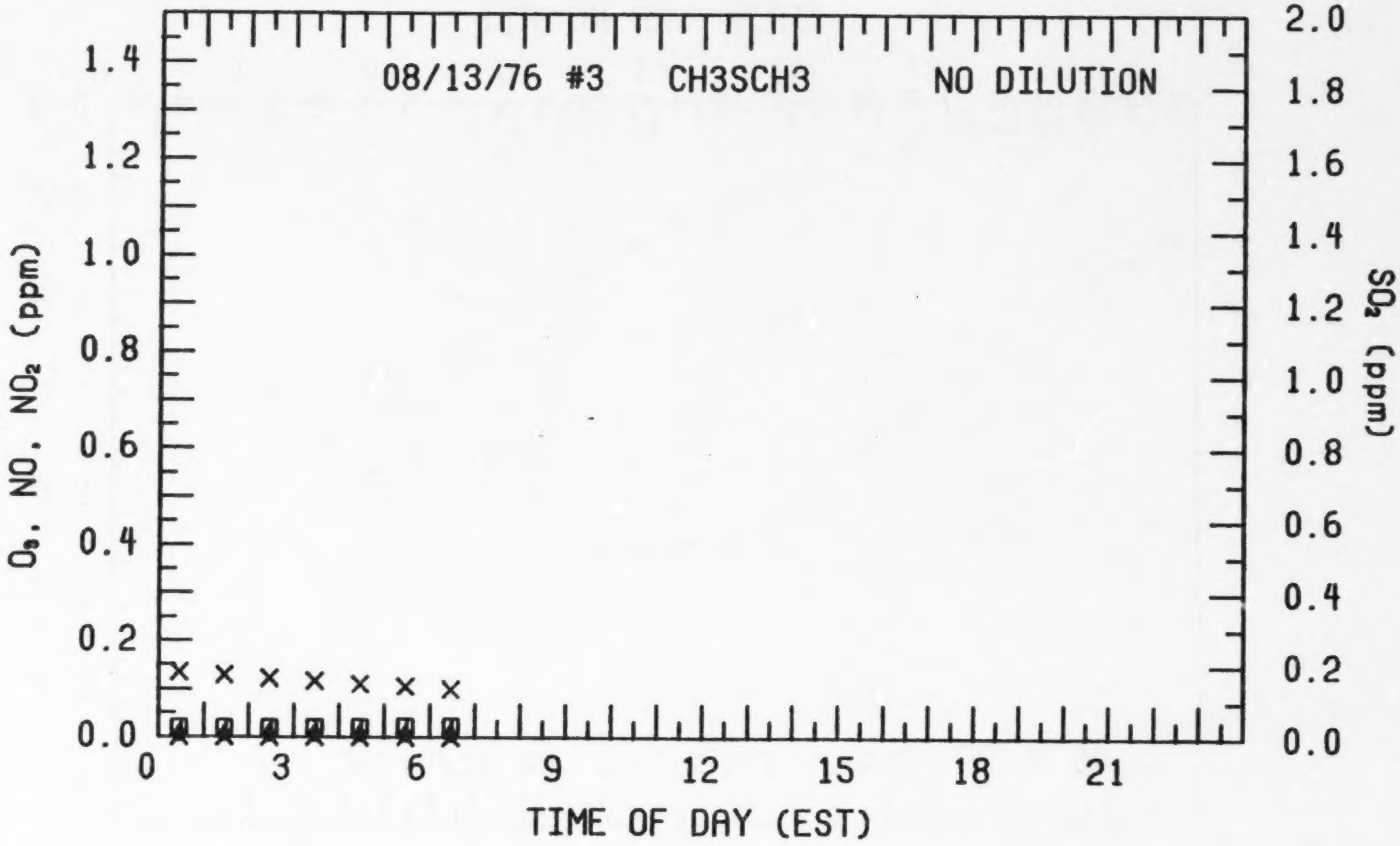
08/12/76 #2
CH3SSCH3
NO DILUTION
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

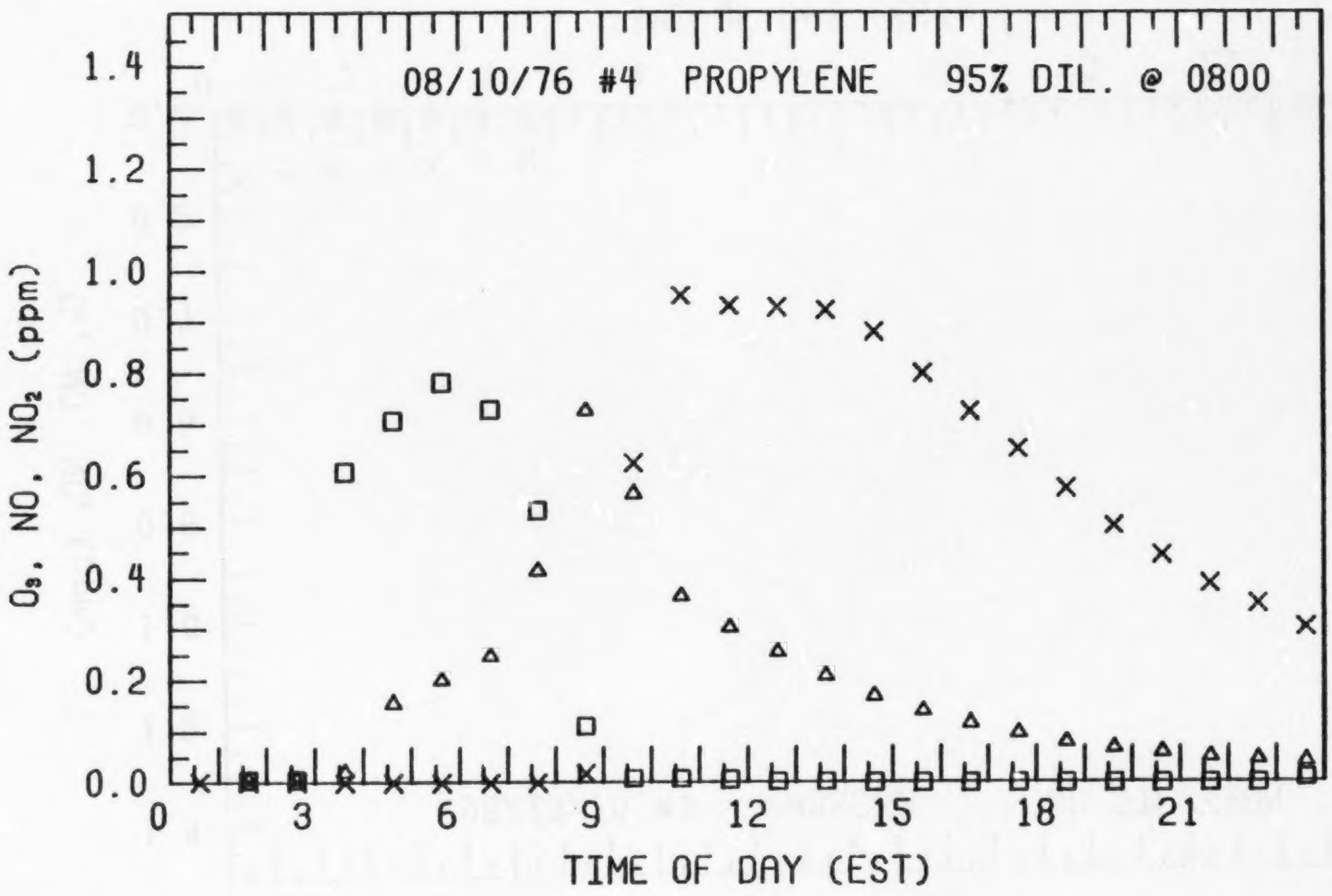

08/13/76 #2 CH3SSCH3 NO DILUTION
O_3, NO, NO_2 (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
SO_2 (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

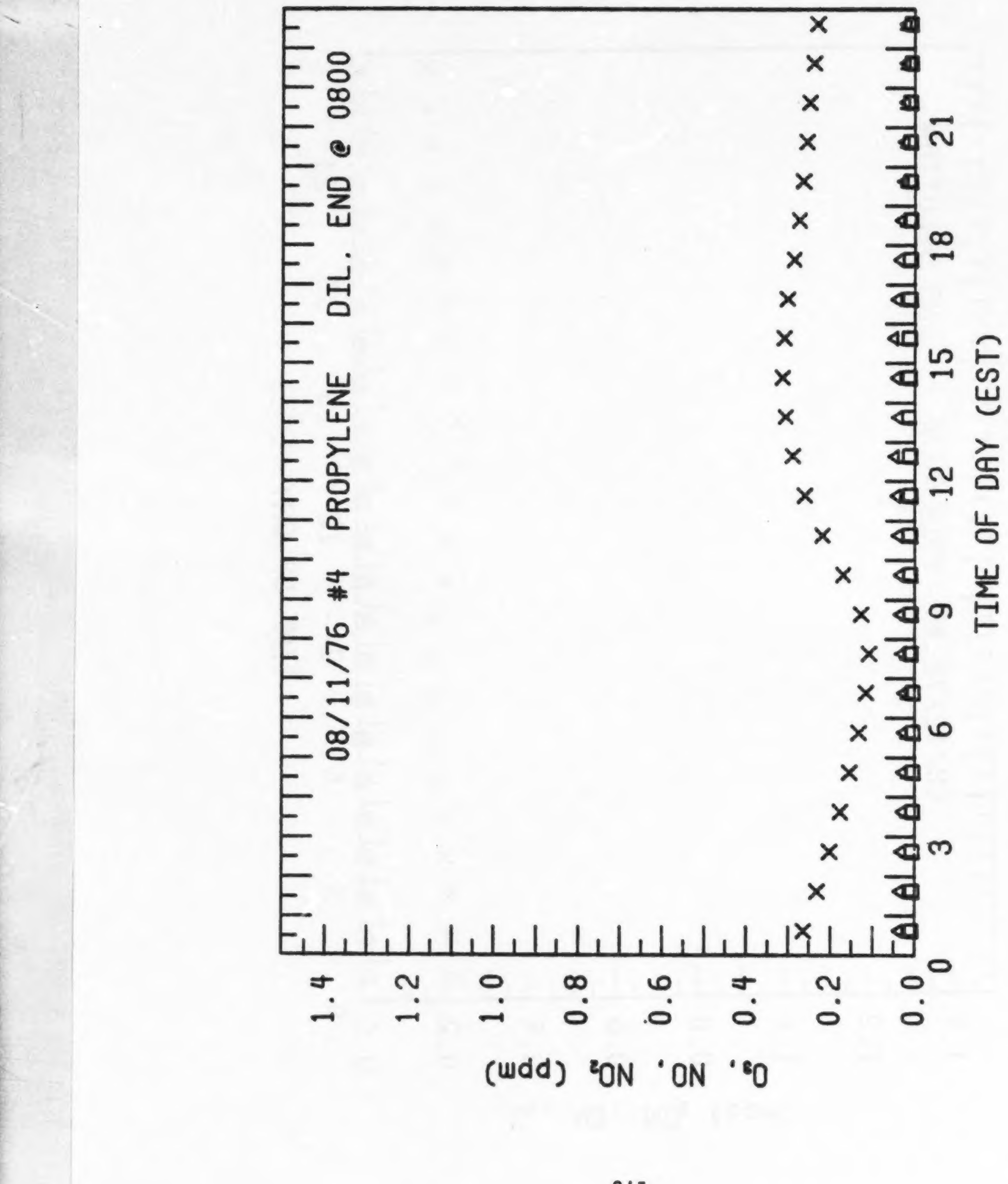

08/10/76 #3
CH3SCH3
95% DIL. @ 0800
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
TIME OF DAY (EST)
0
3
6
9
12
15
18
21

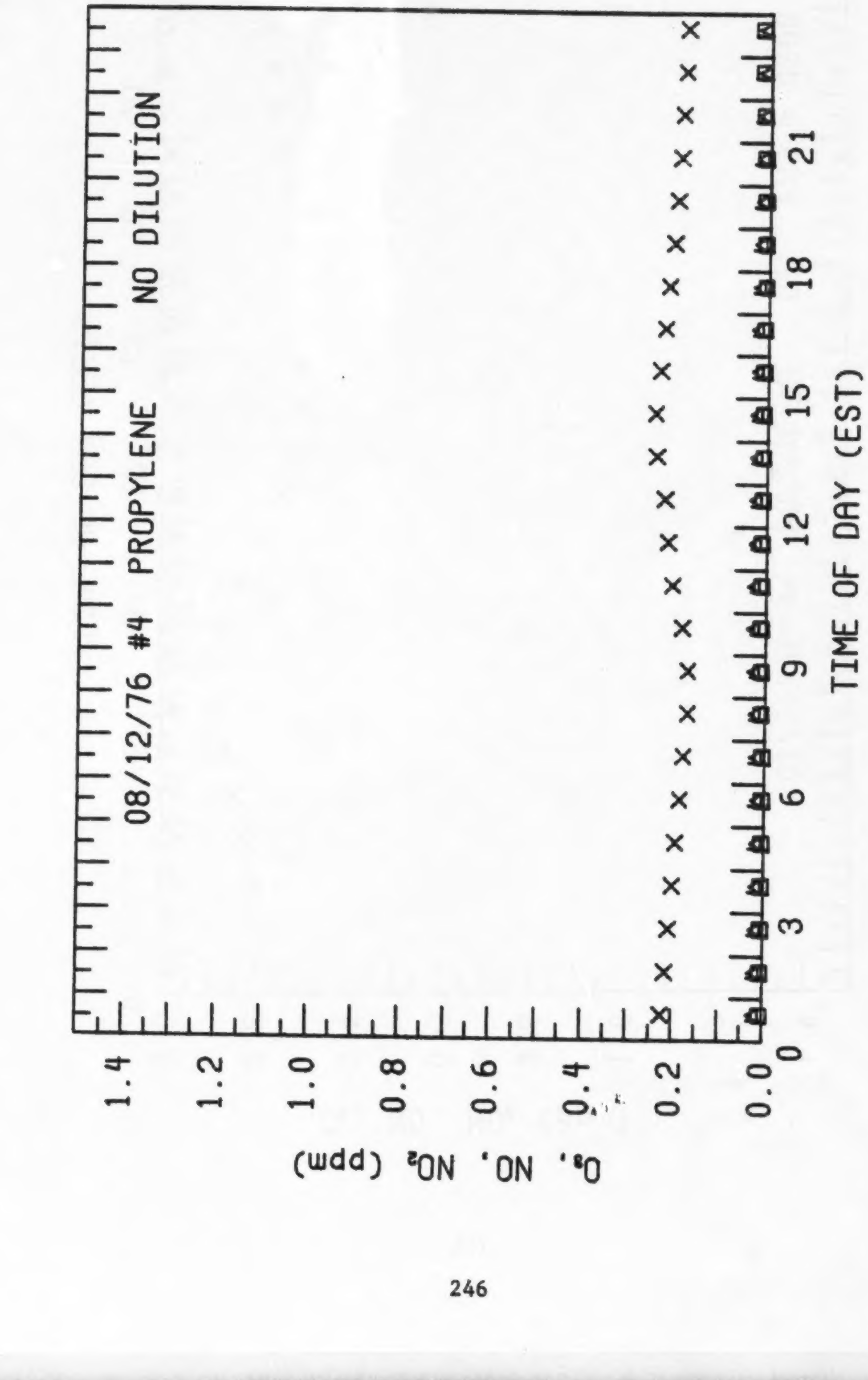

08/11/76 #3 CH3SCH3 DIL. END @ 0800
SO₂ (ppm)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)

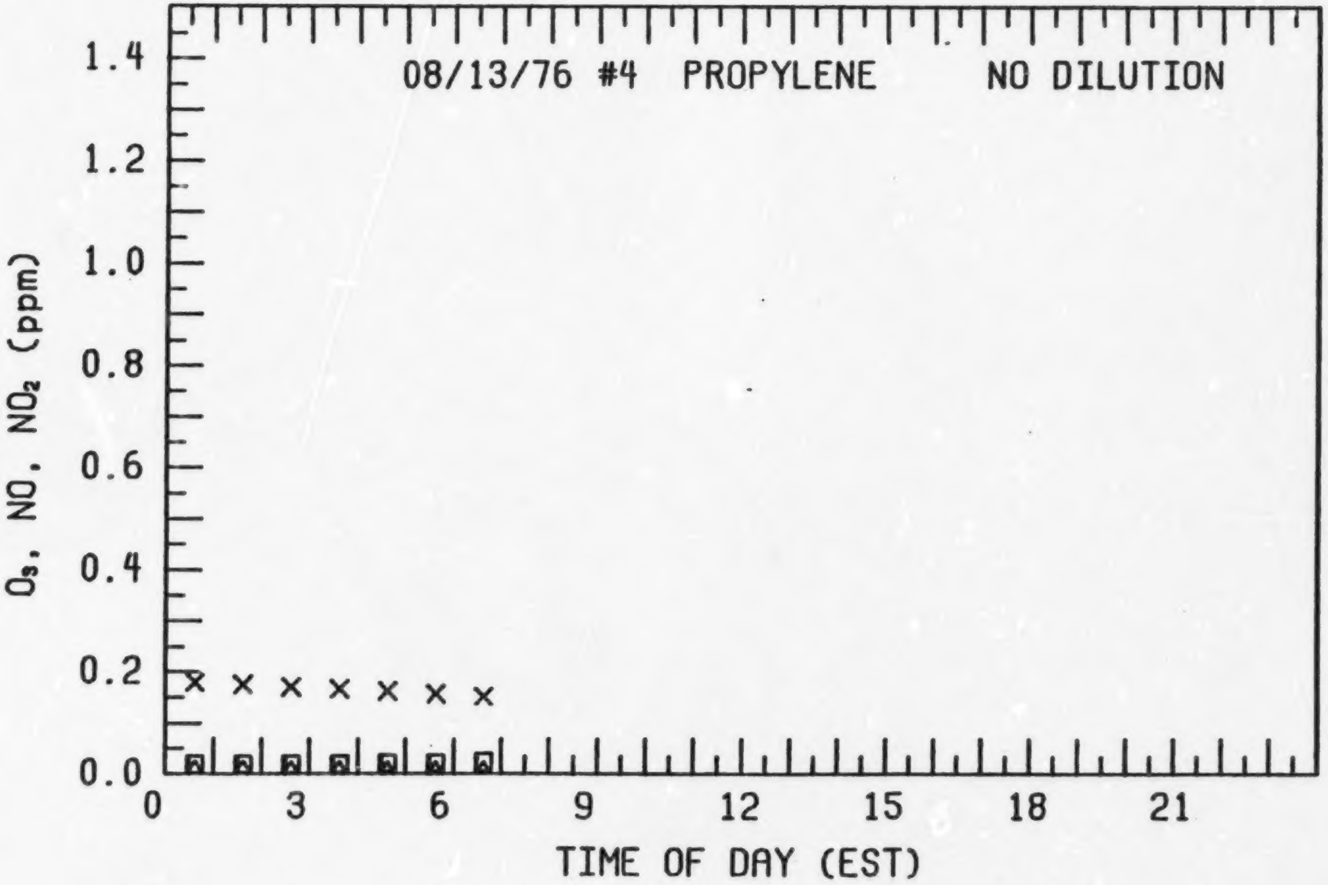

08/12/76 #3 CH3SCH3 NO DILUTION
TIME OF DAY (EST)
0
3
6
9
12
15
18
21
O3, NO, NO2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0


08/13/76 #3 CH3SCH3 NO DILUTION
O_3, NO, NO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
SO_2 (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)


08/10/76 #4 PROPYLENE 95% DIL. @ 0800
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)


08/11/76 #4 PROPYLENE DIL. END @ 0800
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)


08/12/76 #4 PROPYLENE NO DILUTION
O₃, NO, NO₂ (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
TIME OF DAY (EST)
0
3
6
9
12
15
18
21


08/13/76 #4 PROPYLENE NO DILUTION
O₃, NO, NO₂ (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
TIME OF DAY (EST)